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Regional Air Pollution Study Gas Chromatography Laboratory Operations

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The Regional Air Pollution Study (RAPS) is collecting data on a regional scale for the evaluation and further development of air quality simulation models. A gas chromatography laboratory is operated to provide analyses for selected pollutants required to fully assess various submodels included in air quality simulation models. Hydrocarbons and other components of the atmosphere are analyzed in support of such studies as: 1) evaluation and development of submodels concerned with photo-oxidation reactions and transformations in the atmosphere; 2) evaluation of emissions inventory submodels; 3) tracking plumes; and 4) relationship between grid area measurements and grid point measurements. Specifically, atmospheric samples were analyzed for C_1-C_{10} hydrocarbons, CO, NO + NO_2, and total hydrocarbons. Additionally, analytical procedures were prepared and made operational for SO_2, SF_6, fluorocarbon -11, and fluorocarbon - 12. The report describes the preparations and operations of a gas chromatography laboratory for analysis of atmospheric samples. The report includes a work plan, chromatographic sampling and analysis schemes, quality assurance tests and air sample bag storage and contamination tests.

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REGIONAL AIR POLLUTION STUDY:

GAS CHROMATOGRAPHY LABORATORY OPERATIONS

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PART I: ESTABLISHMENT OF THE GAS CHROMATOGRAPH LABORATORY

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1. INTRODUCTION

To accomplish the objectives of the Regional Air Pollution Study (RAPS) it is necessary to perform continuous and selective intensive monitoring and analysis of atmospheric pollutants. The collection and monitoring of these pollutants is performed by the 25 remotely operated Regional Air Monitoring Systems (RAMS) stations, mobile laboratories, airborne laboratories and other bag sample collection techniques. Analysis of the collected atmospheric bag samples is to be performed at the RAPS Central Facility in a gas chromatography laboratory to be established for this purpose. It was the objective of this Task Order to set up and initiate operation of the RAPS Gas Chromatography Laboratory. The following sections of this report present a summary of the initial effort performed under Task Order No. 3 to establish the RAPS Gas Chromatography Laboratory.

2. TASK ORDER REQUIREMENTS

Under this Task Order the contractor was to provide the necessary manpower, materials and services to perform the following:

Services: Establish and operate a gas chromatography laboratory, collect gas samples and perform quantative analysis for nitrogen oxides, carbon monoxide, C_1 to C_{10} hydrocarbons, total hydrocarbons and other organic pollutants. A government furnished Perkin Elmer,Model 900B gas chromatograph with a PEP-1 data system and a Beckman Model 6800 gas chromatograph were to be provided. A government furnished analyzer to perform analysis for nitrogen oxides was also to be provided. Samples were to be collected in Tedlar plastic bags, gas bottles, or absorbing traps. Precautions were to be taken to prevent condensation of vapors in sample bags and sample bottles. Ambient air samples were to be collected continuously for periods ranging from 15 minutes to three hours. Provide EPA with a monthly report containing reduced data.

2. TASK ORDER REQUIREMENTS (CONTINUED)

Personnel: Provide the following personnel; one expert gas chromatographer, one technician experienced in source sampling

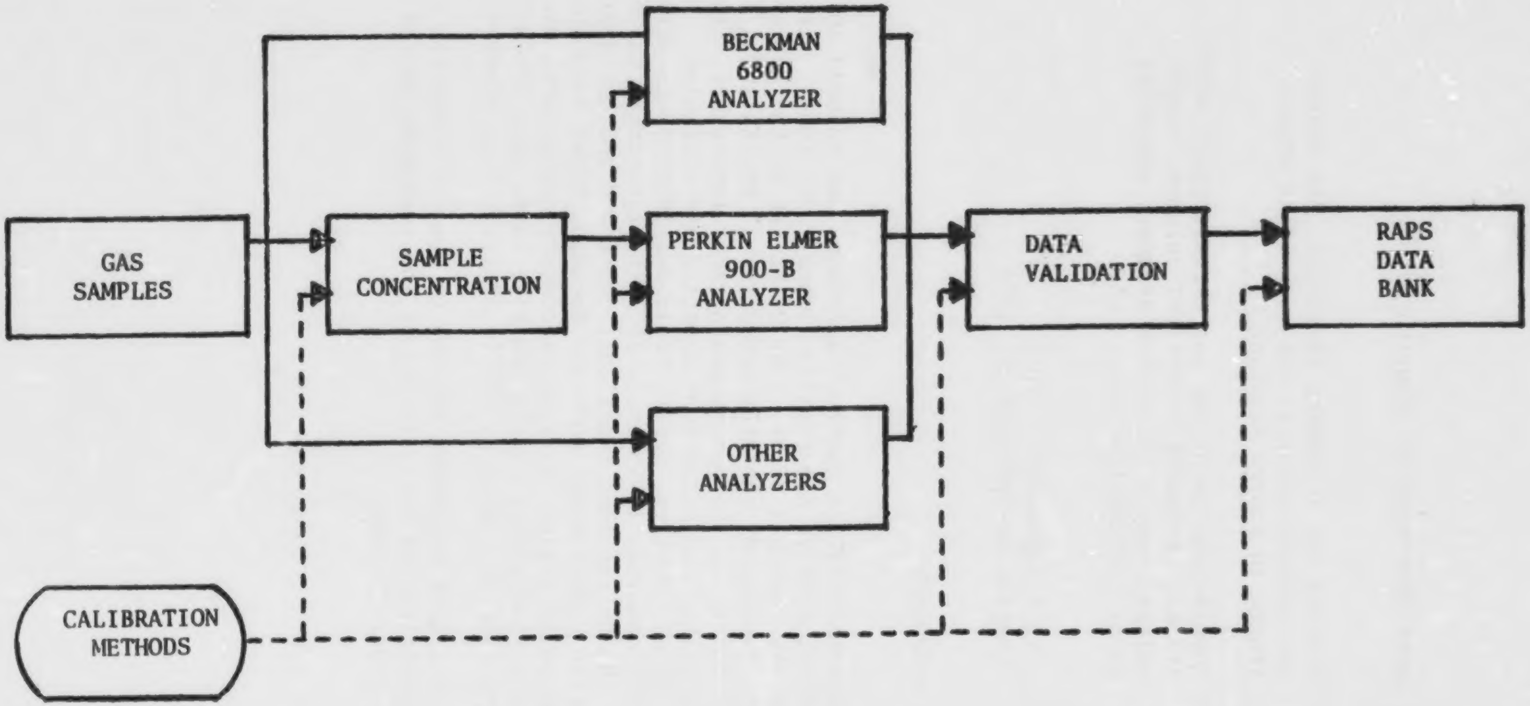
Equipment: Furnish equipment for gas chromatograph operations, including analytical columns, sample valves, sample collection systems, operating gases, calibration mixes, etc.

Period of
Performance: Start-September 1, 1973
Completion-February 28, 1974

3. WORK PERFORMED

In September 1973 a contract agreement was entered into with McDonnell Douglas Electronics Company, St. Louis, Missouri to provide the services of Dr. John Q. Walker as the gas chromatographic expert for the RAPS laboratory. Dr. Walker's first action was to set up the gas chromatography laboratory. The government furnished analyzers were unpacked and assembled. Necessary laboratory supplies, gases, tools and instruments were determined and ordered. In November 1973 the laboratory was established to the degree that functional check out and calibration of the Perkin Elmer, Model 900B and Beckman, Model 6800 chromatographs could begin. Various laboratory operational procedures were studied for sample analysis based upon the methodology depicted in Figure 1, Sample Analysis Flow Diagram.

Specific work performed setting up the gas analyzers for routine operation and analysis during the remaining period of this Task Order follows:


GAS SAMPLES
SAMPLE CONCENTRATION
BECKMAN 6800 ANALYZER
PERKIN ELMER 900-B ANALYZER
OTHER ANALYZERS
DATA VALIDATION
RAPS DATA BANK
CALIBRATION METHODS

SAMPLE ANALYSIS FLOW DIAGRAM

FIGURE 1

3.1 PERKIN ELMER, MODEL 900B CHROMATOGRAPH

The high resolution gas chromatograph system to be set up and made operational was comprised of three major components: 1) Perkin Elmer, Model 900B chromatograph 2) Perkin Elmer, Model PEP-1 Laboratory Computer System and 3) a Houston Omni Scribe, Model 5213-4 dual pen recorder.

The initial objective was to adapt previously developed methods for analysis of atmospheric samples using this dual column instrument to conduct two simultaneous analyses of C_1 through C_{10} hydrocarbons including compound type separations (i.e. saturates from unsaturates and aromatics). Early in the program it was recognized that the existence of a single column with this capability would streamline operations over the multiple column methods previously used (Reference 1 and 2). An additional developmental goal was to establish methods for analyzing key compounds related to the internal combustion engine's contribution to air pollution in concentrations less than 1 ppm (i.e. acetylene, acetaldehyde, and aromatic hydrocarbons).

Dr. Walker's knowledge of the gas chromatograph methods used at the Shell Research Laboratories for analysis of complex hydrocarbons during production of gasoline appeared to offer a unique opportunity applicable to the needs of the RAPS program. It was not fully recognized at the outset however, that the hydrocarbon composition of gasoline samples differed from atmospheric samples. Atmospheric sample complexity is increased because of the presence of reasonably large quantaties of both polar and non-polar compounds; water, aldehydes and alcohol are typical examples.

Early attempts to place the system in operation were confronted with several problems:

1) Late delivery of required laboratory equipment for the sample injection system (solenoid valves, valve oven, fittings, absolute pressure gauge, molecular sieve, etc.).

2) The Perkin Elmer service representative had to be called in to repair both the PE 900Bchromatograph and PEP-1 computer.

3) Late delivery of gases for preparation of standards,etc.

3.1.1 COLUMN SELECTION FOR ANALYSIS OF C_1 - C_{10} WITH THE PE900B

During November and December 1973 literature surveys were made in conjunction with experimental tests to define and verify procedures for routine sample analysis of C_1 thru C_{10} hydrocarbons utilyzing a single column. The results of this effort determined that adequate separation and resolution for reasonable analysis times could not be achieved. For example, Shell Oil uses a 200 ft. x 0.01 inch I.D. squalane column, temperature programmed from -5 to 95° C. The disadvantages of this method are the very long sample analysis time and poor separation of the C_1 - C_4 compounds. A typical chromatogram for hydrocarbon identification performed by the Shell Research Laboratories is presented in Figure 2 and Table 1.

A test was run on the PE900B using a 150 ft. x 0.02 inch I.D. support-coated open tubular squalane column programmed over a 0° to 90° C temperature range. A analysis (75 min) of both natural gas and the C_3 - C_{12} hydrocarbons of full range gasoline was achieved. With this success, development of a method for concentrating atmospheric samples was initiated.

3.1.2 SAMPLE CONCENTRATION DEVELOPMENT

Following meetings with W.A. Lonneman, Chromatography Laboratory, EPA, Research Triangle Park, North Carolina and others, it was decided to evaluate a sampling trap with concentration capability similar to that developed by T.A. Bellar, EPA, Cincinnati, Ohio.

Materials were ordered and a trap constructed of 18 inch x 1/4 inch O.D. stainless steel containing 5 cm of OY-17 on chromosorb, 15cm of silica gel, 10 cm of 13A molecular sieve and 10 cm of 5A molecular sieve. This column required 3 to 5 minutes for desorption at 225° C which is too slow. Furthermore, the size of the column was not compatible with high resolution gas chromatography. A similar column made of 1/8 inch stainless steel was fabricated and similar unsatisfactory performance characteristics were found.

FIGURE 2

CHROMATOGRAM OF AUTOMOBILE EXHAUST GAS OPERATED WITH PREMIUM LEADED FUEL

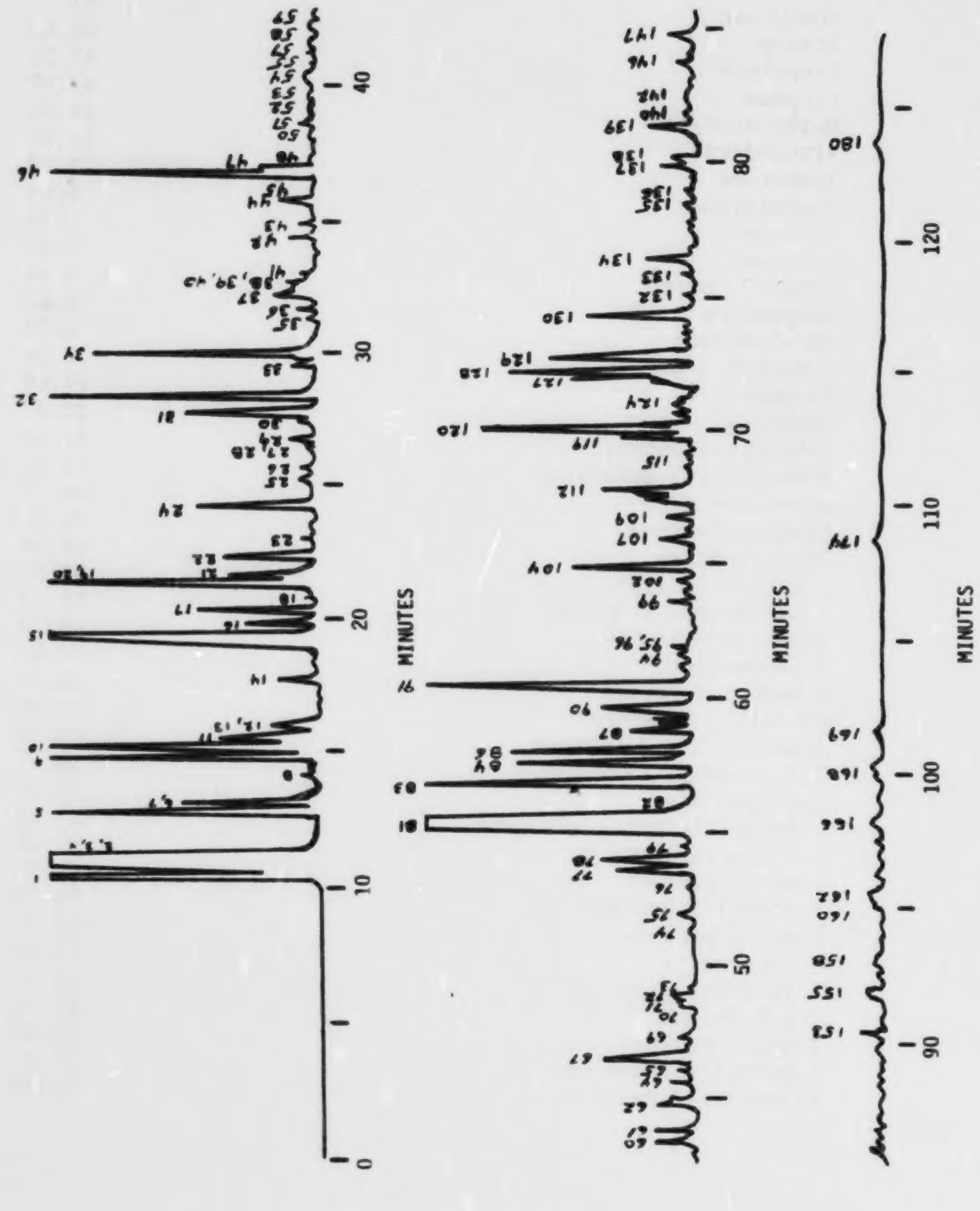


TABLE 1-A

PEAK NUMBER	COMPONENT	BOILING POINT, °C
1	Methane	161.49
2	Ethylene	103.71
3	Acetylene	84
4	Ethane	88.63
5	Propylene	47.70
6	Propane	42.07
7	Methylacetylene	23.22
	+Propadiene	34.5
8	Isobutane	11.73
9	Isobutylene	6.90
	+Butene-1	6.26
10	n-Butane	0.50
11	Trans-2-Butene	0.88
12	Neopentane	9.50
13	Cis-2-Butene	3.72
14	3-Methyl-1-Butene	20.06
15	Isopentane	27.85
16	Pentene-1	29.97
17	2-Methyl-1-Butene	31.16
18	2-Methyl-1,3-Butadiene	34.07
19	n-Pentane	36.07
20	Trans-2-Pentene	36.33
21	Cis-2-Pentene	36.94
22	2-Methyl-2-Bitene	38.57
23	3,3-Dimethyl-1-Butene	41.24
24	2,2-Dimethylbutane	49.74
25	Cyclopentene	44.24
26	3-Methyl-1-Pentene	54.14
	+4-Methyl-1-Pentene	53.88
27	4-Methyl-Cis-2-Pentene	56.30
28	2,3-Dimethyl-1-Butene	55.67
29	Cyclopentane	49.26
30	4-Methyl-1-Trans-2-Pentene	58.55
31	2,3-Dimethylbutane	57.99
32	2-Methylpentane	60.27
33	2-Methyl-1-Pentene	60.72
34	3-Methylpentane	63.28
	+ (Hexene-1)	63.49
	+ (2-Ethyl-1-Butene)	64.66
35	Cis-3-Hexene	66.47
36	Trans-3-Hexene	67.08
37	3-Methylcyclopentene	65.0
	+2-Methyl-2-Pentene	67.29

TABLE 1-B

PEAK NUMBER	COMPONENT	BOILING POINT, °C
38	3-Methyl-Cis-2-Pentene	67.70
39	n-Hexane	68.74
	+ (4,4-Dimethyl-1-Pentene)	72.49
40	Trans-2-Hexene	67.87
41	Cis-2-Hexene	68.84
42	3-Methyl-Trans-2-Pentene	70.44
43	4,4-Dimethyl-Trans-2-Pentene	76.75
44	Methylcyclopentane	71.81
	+ 3,3-Dimethyl-1-Pentene	77.57
45	2,2-Dimethylpentane	79.20
	+ 2,3-Dimethyl-2-Butene	73.21
	+ (2,3,3,-Trimethyl-1-Butene)	77.87
46	Benzene	80.10
47	2,4-Dimethylpentane	80.50
48	4,4-Dimethyl-Cis-2-Pentene	80.42
49	2,2,3-Trimethylbutane	80.88
50	2,4-Dimethyl-1-Pentene	81.64
51	1-Methylcyclopentene	75.8
	+ 2-Methyl-Cis-3-Hexene	86
52	2,4-Dimethyl-2-Pentene	83.26
	+ 3-Ethyl-1-Pentene	84.11
	+ 3-Methyl-1-Hexene	84
53	2,3-Dimethyl-1-Pentene	84.28
54	2-Methyl-Trans-3-Hexene	86
	+ 5-Methyl-1-Hexene	85.31
55	3,3-Dimethylpentane	86.06
56	Cyclohexane	80.74
	+ (4-Methyl-Cis-2-Hexene)	87.31
57	4-Methyl-1-Hexene	86.73
	+ 4-Methyl-Trans-2-Hexene	87.56
58	3-Methyl-2-Ethyl-1-Butene	86.1
	+ 5-Methyl-Trans-2-Hexene	88.11
59	Cyclohexene	82.98
60	2-Methylhexane	90.05
	+ (5-Methyl-Cis-2-Hexene)	89.5
61	2,3-Dimethylpentane	89.78
	+ (1,1-Dimethylcyclopentane)	87.85
	+ (3,4-Dimethyl-Cis-2-Pentene)	87.9
62	3-Methylhexane	91.85
63	1-Cis-3-Dimethylcyclopentane	91.73
	+2-Methyl-1-Hexene	91.95
	+ 3,4-Dimethyl-Trans-2-Pentene	90.5
64	1-Trans-3-Dimethylcyclopentane	90.77
	+1-Heptene	93.64
	+2-Ethyl-1-Pentene	94

TABLE 1-C

PEAK NUMBER	COMPONENT	BOILING POINT, °C
65	3 Ethylpentane	93.48
	+3-Methyl-Trans-2-Hexene	94
66	1-Trans-2-Dimethylcyclopentane	91.87
67	2,2,4-Trimethylpentane	99.24
	+ (Trans-3-Heptene)	95.67
68	Cis-3-Heptene	95.75
69	3-Methyl-Cis-3-Hexene	95.33
	+2-Methyl-2-Hexene	95.44
	+3-Methyl-Trans-3-Hexene	93.53
70	3-Ethyl-2-Pentene	96.01
71	Trans-2-Heptene	97.95
72	n-Heptane	98.43
	+ (3-Methyl-Cis-2-Hexene)	94
73	2,3-Dimethyl-2-Pentene	97.40
	+ Cis-2-Heptene	98.5
74	1-Cis-2-Dimethylcyclopentane	99.57
75	Methylcyclohexane	100.93
	+2,2-Dimethylhexane	106.84
	+ 1,13-Trimethylcyclopentane	104.89
76	4-Methylcyclohexene	102.74
77	2,5-Dimethylhexane	109.10
	+ Ethylcyclopentane	103.47
78	2,4-Dimethylhexane	109.43
79	2,2,2,-Trimethylpentane	109.84
80	1-Trans-2-Cis-4-Trimethylcyclopentane	109.29
81	Toulene	110.63
	+3,3-Dimethylhexane	111.97
82	1-Trans-2-Cis-3-Trimethylcyclopentane	110.2
83	2,3,4-Trimethylpentane	113.47
84	2,3,3-Trimethylpentane	114.76
85	1,1,2-Trimethylcyclopentane	113.73
86	2,3-Dimethylhexane	115.61
	+2-Methyl-3-Ethylpentane	115.65
87	2-Methylheptane	117.65
88	4-Methylheptane	117.71
89	3,4-Dimethylhexane	117.73
	+ (1-Cis-2-Trans-4-Trimethylcyclopentane)	116.73
90	3-Methylheptane	118.93
	+ (3-Methyl-3-Ethylpentane)	118.26
91	2,2,5-Trimethylhexane	124.08
	+ (1-Cis-2-Cis-4-Trimethylcyclopentane)	118
92	1,1-Dimethylcyclohexane	119.54
	+1-Trans-4-Dimethylcyclohexane	119.35
93	1-Cis-3-Dimethylcyclohexane	120.09
94	1-Methyl-Trans-3-Ethylcyclopentane	120.8
95	2,2,4-Trimethylhexane	126.54

TABLE 1-D

PEAK NUMBER	COMPONENT	BOILING POINT, °C
96	1-Methyl Trans-2-Ethylcyclopentane	121.2
	+1-Methyl-Cis-3-Ethylcyclopentane	121.4
97	Cycloheptane	118.79
	+ 1-Methyl-1-Ethylcyclopentane	121.52
98	1-Trans-2-Dimethylcyclohexane	123.42
	+ 1-Cis-2-Cis-3-Trimethylcyclopentane	123.0
99	n-Octane	125.67
100	1-Cis-4-Dimethylcyclohexane	124.32
101	1-Trans-3-Dimethylcyclohexane	124.45
102	2,4,4 -Trimethylhexane	130.65
103	Isopropylcyclopentane	126.42
104	2,3,5-Trimethylhexane	131.34
105	2,2-Dimethylheptane	132.69
106	1-Methyl-Cis-2-Ethylcyclopentane	128.05
107	2,4-Dimethylheptane	133.5
	+ 2,2,3-Trimethylhexane	133.6
108	2,2-Dimethyl 3 Ethylpentane	133.83
	+ 2-Methyl-4-Ethylhexane	133.8
109	2,6-Dimethylheptane	135.21
	+ (1-Cis-2-Dimethylcyclohexane)	129.73
110	n-Propylcyclopentane	130.95
111	Ethylcyclohexane	131.78
	+ 2,5-Dimethylheptane	136.0
	+ 3,5-Dimethylheptane	136.0
112	Ethylbenzene	136.19
113	2,4-Dimethyl-3-Ethylpentane	136.73
114	3,3-Dimethylheptane	137.3
115	1,1,3-Trimethylcyclohexane	136.63
116	2,3,3-Trimethylhexane	137.68
117	1-Cis-3-Cis-5-Trimethylcyclohexane	138.41
118	2-Methyl-3-Ethylhexane	138.0
119	p-Xylene	138.35
120	m-Xylene	139.10
	+ (3,3,4-Trimethylhexane)	140.46
121	2,3-Dimethylheptane	140.5
122	3,4-Dimethylheptane	140.6
123	4-Methyloctane	142.48
124	2-Methyloctane	143.26
125	3-Ethylheptane	143.0
126	3-Methyloctane	144.18
127	O-Xylene	144.41
	+ (2,2,4,5-Tetramethylhexane)	147.88
128	2,2,4-Trimethylheptane	147.8
129	2,2,5-Trimethylheptane	148
	+ 2,2,6-Trimethylheptane	148

TABLE 1-E

PEAK NUMBER	COMPONENT	BOILING POINT, °C
130	2,5,5-Trimethylheptane	152.80
	+ 2,4,4-Trimethylheptane	153
131	Isopropylbenzene	152.39
132	n-Nonane	150.80
133	3,3,5-Trimethylheptane	155.68
134	2,4,5-Trimethylheptane	157
	+2,3,5-Trimethylheptane	157
135	n-Proplybenzene	159.22
136	2,2,3,3-Tetramethylhexane	160.31
	+ 2,6-Dimethyloctane	158.54
137	1-Methyl-3-Ethylbenzene	161.31
138	1-Methyl-4-Ethylbenzene	161.99
139	3,3,4-Trimethylheptane	164
	+ 3,4,4-Trimethylheptane	164
	+ 3,4,5-Trimethylheptane	164
140	1-Methyl-2-Ethylbenzene	165.15
	+ 5-Methylnonane	165.1
141	4-Methylnonane	165.7
142	1,3,5-Trimethylbenzene	164.72
143	2-Methylnonane	166.8
144	Tert-Butylbenzene	169.12
145	3-Methylnonane	167.8
146	Unidentified C_{10} Alkylate Peak	
147	1,2,4-Trimethylbenzene	169.35
148	Sec-Butylbenzene	173.31
	+ Isobutylbenzene	172.76
149	1-Methyl-3-Isopropylbenzene	175.14
150	n-Decane	174.12
151	1,2,3-Trimethylbenzene	176.08
	+1-Methyl-4-Isopropylbenzene	177.10
152	1-Methyl-2-Isopropylbenzene	178.15
	+ Indane	177
153	Unidentified C_{11} Alkylate Peak	
154	1,3-Diethylbenzene	181.10
155	Unidentified C_{11} Alkylate Peak	
156	1-Methyl-3-n-Propylbenzene	181.80
157	n-Butylbenzene	183.27
158	1,2-Diethylbenzene	183.42
	+ 1-Methyl-4-n-Propylbenzene	183.75
159	1,4-Diethylbenzene	183.30
160	1-Methyl-2-n-Propylbenzene	184.80
161	1,3-Dimethyl-5-Ethylbenzene	183.75
162	Unidentified C_{11} Alkylate Peak	
163	2-Methylindane	184
164	1,4-Dimethyl 2-Ethylbenzene	186.91
165	1-Methylindane	186.5

TABLE 1-F

PEAK NUMBER	COMPOUND	BOILING POINT, °C
166	1-Methyl-3-Tert-Butylbenzene +Unidentified C_{11} Alkylate Peak	189.26
167	1,3-Dimethyl-4-Ethylbenzene	188.41
168	1,3-Dimethyl-2-Ethylbenzene + 1,2-Dimethyl-4-Ethylbenzene	190.01 189.75
169	1-Methyl-4-Tert-Butylbenzene + Unidentified C_{11} Alkylate Peak	192.76
170	1,2-Dimethyl-3-Ethylbenzene	193.91
171	n-Undecane	195.89
172	1,2,4,5-Tetramethylbenzene	196.8
173	1,2,3,5-Tetramethylbenzene	198.0
174	Isopentylbenzene	198.9
175	5-Methylindane	199
176	4-Methylindane	203
177	n-Pentylbenzene	205.46
178	1,2,3,4-Tetramethylbenzene	205.4
179	Tetraline	205.57
180	Naphthalene	217.96
181	1,3-Dimethyl-5-Tert-Butybenzene	205.1
182	n-Dodecane	216.28

( ) Designates minor component

To overcome the long desorption time and improve the resolution a two step concentration procedure was next implemented. The 18 inch x 1/4 inch concentration column (previously discussed) was interfaced to a smaller volume (20 inch x 0.02 inch I.D.) column coated with OV101 silicone oil and cooled to liquid nitrogen temperature. The effluent from this concentration column was then fed into the squalane analytical column. This concentration configuration was set up for evaluation using the following analysis conditions and procedures:

1) Isothermal at 0° for 12 minutes, then

2) Temperature programmed at 2° C to 90° C, then

3) Flow programmed at 1 pound per minute from 15 to 40 psig.

4) Eighty minutes (± 15 sec.) are required for the elution of normal decane. Following this the column flow is reversed (opening the back flush valve) to elute the "nC_{10} plus" flaction.

Just prior to initiation of testing with this configuration, the squalane column deteriorated to an unusable point. Normal procedures were tried to regenerate the column efficiency with no success.

Procurement of a replacement 200 ft. x 0.02 inch I.D. was initiated. This concluded the effort performed on the PE 900B chromatograph analysis development during the period of performance on this Task Order.

3.2 BECKMAN, MODEL 6800 CHROMATOGRAPH

Initial operation and check out of this instrument began in November 1973. Due to damage received during shipment the instrument would not separate C_2 hydrocarbons (ethane, ethylene and acetylene). A Beckman service engineer was called in and the unit repaired. Several printed circuit boards were found out of alignment with their connectors and the molecular sieve column was partially deactivated.

Check out and calibration of the chromatograph was next initiated. A 140 ft^3 gas blend of 45 ppm CO, 5 ppm CH_4, 5 ppm C_2H_4 and 5 ppm C_2H_2 in nitrogen was prepared to be used as a reference standard with a commercially prepared 5 ppm CH_4 in nitrogen mixture.

Early analysis results showed very poor repeatability. The problem was found to be caused by a contaminated cylinder of ultra pure hydrogen. The was replaced with a new cylinder and satisfactory operation was then achieved.

4. SUMMARY

During the six month period covered by this Task Order the RAPS, St. Louis, Gas Chromatography Laboratory was established. The services of a professional gas chromatographer, Dr. John Q. Walker were acquired. Equipment and supplies were procured to support laboratory operations. Two analyzers were set up and tests initiated to establish operational procedures for sample insertion techniques.

Plans were developed for a one year follow on to this initial gas chromatography laboratory effort. A schedule was developed to place the laboratory in operation and begin routine sample bag analysis in the near future. Additional laboratory staffing and equipment procurement was also planned.

References

1. "Analysis of the Atmosphere for Light Hydrocarbons," by Edgar R. Stephens and Frank R. Burleson; Journal of the Air Pollution Control Association, (March 1967)

2. "Hydrocarbon Composition of Urban Air Pollution," by W.A. Lonneman, S.L. Kopczynski, P.E. Darley and F.D. Sutterfield; Environmental Science and Technology, (March 1974)

PART II: OPERATIONAL PROCEDURES

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1.0 INTRODUCTION

To accomplish the objectives of the Regional Air Pollution Study (RAPS), it is necessary to perform both continuous and selective intensive periodic monitoring of atmospheric pollutants. The gas chromatography laboratory located within the RAPS Central Facility has been established to support a variety of studies under the RAPS program. The laboratory will assist in the evaluation of the Regional Air Monitoring System (RAMS) station performance, validation of automotive emissions inventory submodels, defining the composition of emissions from significant sources, tracking plumes, and developing and validating photochemical submodels, particularly those involving the contribution of the hydrocarbon-nitrogen oxide atmospheric reaction system to the photoxidation of sulfur dioxide to sulfate.

The gas chromatography laboratory collects and analyzes atmospheric samples for a variety of pollutants, including hydrocarbons, carbon monoxide, and atmospheric tracer gases. Supplemental analyses for sulfur compounds and nitrogen-oxides are also to be run on many samples using government furnished analyzers.

Data from all analyses are recorded and entered into the RAMS/RAPS computer data bank.

The objective of the task order was to continue with the establishment of the gas chromatography laboratory and develop operational procedures previously initiated by Task Order No. 3. The following sections of this report present a summary of the work performed under Task Order No. 21, Gas Chromatography Laboratory Operation.

2.0 TASK ORDER REQUIREMENTS

Under this task order the contractor was to provide the necessary manpower, materials and services to perform a variety of studies as directed by the RAPS Field Coordinator. A summary of specific activities to be performed is presented in the following task specification:

2.1 SERVICES

1. The contractor shall prepare and submit to the RAPS Field Coordinator for approval a work plan for operation of the Gas Chromatography Laboratory. The plan shall include schedules, man-power estimates, and milestones for bringing the gas chromatography lab into a state of complete readiness for analysis of atmospheric samples. The work plan shall include the operation and calibration of all government furnished (GFE) instruments, data processing, analysis, and reporting. It shall also consider the entry and retrieval of data into/from the RAMS/RAPS data bank.

2. The contractor shall develop analytical configurations and methods for gas chromatographic analysis of atmospheric samples for C_1 - C_{10} hydrocarbons, CO, methyl mercaptan, and atmospheric tracer gases, such as SF_6 and fluorocarbons. Except for methane, hydrocarbons must be measured at concentrations down to one part per billion carbon (ppb C). Sulfur compounds to 0.1 ppb, and tracer gases to 1 part per trillion.

3. Sampling shall be done at the RAMS monitoring stations, from helicopters, from mobile vehicles, and at various sites in the St. Louis area. The contractor shall pick up and deliver to the gas chromatography lab all bag samples collected at the RAMS stations. The bags shall be shielded from sunlight during pickup and delivery. The contractor shall replace filled bags at the RAMS stations with clean, leak-tight bags.

4. The contractor shall concentrate and analyze atmospheric samples for specific experiments conducted by RAPS investigators.

5. The contractor shall analyze about 400 or more atmospheric samples for individual hydrocarbons (C_1 - C_{10} inclusive), total nonmethane hydrocarbons (NMHC), CO, NO, and NO_x. Of these samples, the contractor shall additionally analyze 100 of the samples for H_2S, SO_2, total sulfur, and methyl mercaptan; and for atmospheric tracer gases (SF_6, fluorocarbons).

6. The contractor shall validate all analyses, record and report concentrations for all chemical species specified above as well as sum of paraffins less methane, sum of olefins, and sum of aromatics.

7. The contractor shall operate all laboratory equipment, and perform instrument calibrations, routine service, and maintenance. EPA will provide necessary replacement of major parts and emergency services normally performed by instrument manufacturers for all GFE instruments.

8. The contractor shall provide all necessary administrative and operational support for contract personnel assigned to this task.

9. The contractor shall provide each month a technical and financial progress report.

2.2 PERSONNEL

1. The contractor is to provide the following personnel as a minimum:
    a. One expert gas chromatographer.
    b. One laboratory technician experienced in quantitative analysis of gases.

2.3 EQUIPMENT

The contractor shall furnish all necessary equipment and supplies required for efficient and effective operation of the gas chromatography laboratory.

2.4 PERIOD OF PERFORMANCE

Start 1 March 1974
Completion 30 November 1974

3.0 WORK PERFORMED

At the time of initiation of effort on this task order, the gas chromatography laboratory was still in the early stages of development. Laboratory tools, supplies and equipment were still being procured.

Instruments and analyzers were still being received, set up in the laboratory and operational methods and procedures developed. The Perkin Elmer, Model 900 B Chromatograph had been set up with its companion Perkin Elmer, PEP-1 Computer and dual pen recorder. This chromatograph, however, still required considerable development work to establish the capability for routine C_1 through C_{10} hydrocarbon analysis. The Beckman Model 6800 Chromatograph had been set up, calibrated and was ready to start routine analysis.

The activity that transpired for nine months in support of this task order follows:

3.1 PERSONNEL

In early March 1974 a new contract agreement was entered into with McDonnell Douglas Electronics Company, St. Louis, Missouri for the continued services of John Q. Walker. Mr. Walker would continue to serve as the senior gas chromatographer. In May 1974 Mr. Raymond Mindrup was hired as the gas chromatographer engineer for the laboratory. A part time laboratory technician was hired in April to assist in the laboratory as required. This completed the staffing of the laboratory for the period of this task effort.

3.2 LABORATORY EQUIPMENT

1. The analyzers to be used in the laboratory were all government furnished equipment (GFE) consisting of the following major instruments:

   a. Perkin Elmer, Model 900 Chromatograph
   b. Beckman, Model 6800 Chromatograph
   c. Varian, Model 940, Gas Chromatograph
   d. Bendix, Model 8101-B, NO_X Analyzer

e. Tracor, Model 270, Sulfur Chromatograph
f. Bendix Pure Air System
g. Bendix Dynamic Calibration System

2. The necessary equipment and supplies required for operation of the gas chromatography laboratory were to be provided for by this task order. Throughout the period of performance various supplies, tools and laboratory equipments were procured consisting of:

a. Operating Gases
b. Analytical Columns
c. Valves and Regulators
d. Gas Concentration Systems
e. Flow Meters
f. Miscellaneous Materials as Required

3.3 WORK PLAN

A work plan was to be developed describing the procedures used to perform analysis with each instrument, instrument calibration methods, data processing and data entry and retrieval with the RAPS data bank. Throughout the period of this task order, the major emphasis was placed on setting up the laboratory instruments and preparing them for routine operational use. The next priority was given to the performance of routine analysis of bag samples brought in from the field. The early operational analysis and calibration techniques used were continually being developed and changed as experience with each system was gained. Also, during the period of this task order, analysis techniques for all components had not been fully developed. For the above reasons, very little effort was expended preparing a work plan. The preliminary draft of a work plan was prepared; however, it was not used due to its incomplete status.

3.4 GAS CHROMATOGRAPHIC ANALYSIS DEVELOPMENT

Analytical configurations and methods for gas chromatographic analysis of atmospheric samples for C_1 - C_{10} hydrocarbons, CO, methyl mercaptan, and gases such as SF_6 and fluorocarbons were to be developed using the GFE analyzers described in section 3.2. Supplemental analysis for sulfur compounds and nitrogen oxides were also to be performed. The work performed on each of these analyzers during the period of this task order is described in the paragraph which follows.

3.4.1 Perkin Elmer, Model 900 B Chromatograph

The high resolution gas chromatograph system set up and used for hydrocarbon analysis is comprised of three major components: 1) Perkin Elmer, Model 900 B Chromatograph, 2) Perkin Elmer, Model PEP-1 Laboratory Computer System and 3) Houston Omni Scribe, Model 5213-4 Dual Pen Recorder. C_1 - C_{10} hydrocarbon analysis was to be performed using a dual column system consisting of two 200 ft. squalane SCOT capillary columns. It was planned that each column would be set up the same to enable two simultaneous analyses of C_1 - C_{10} compounds.

At the time effort was initiated on this task order, the chromatograph system was in the process of being modified. A concentration trap(1) had been constructed and tested, made up of 18 inch x 1/4 inch OD stainless steel containing 5 cm of OV-17 on chromosorb, 15 cm of silica gel, 10 cm of 13A molecular sieve and 10 cm of 5A molecular sieve. This column configuration required 3 to 5 minutes of desorption at 225^o which is too slow and not compatible with high resolution gas chromatography. Next a series of tests were initiated using a 150 ft. x 0.02 inch I.D. squalane column(2). No quantitative results were possible from these tests due to a defective column. A replacement 200 ft. x 0.02 inch squalane column was ordered in April 1974.

The initial work performed by this task order on the Perkin Elmer 900 Gas Chromatograph was to continue with the development of columns and trapping techniques to conduct two C_1 to C_{10} hydrocarbon analyses simultaneously on this dual column instrument.

C_1 methane analysis using the PE 900 Chromatograph was dropped as a requirement for this instrument for the following reasons:

1. No efficient method of trapping is possible using liquid oxygen sample concentration traps.

2. The Beckman 6800 Gas Chromatograph can perform specific methane analysis with high resolution and sensitivity in a short sampling period.

3.4.1.1 Column Development

Four support coated open tubular columns were evaluated for separation of hydrocarbon compounds in the C_2 to C_{10} range. Separation and temperature stability performance for each of the tested columns were as follows:

Liquid Phase	Separation	Temp Analysis Limits
Polyphenyl ether(3)	good for aromatics	good to 200°C
Carbowax 1540	good for aromatics	good to 150°C
OV101 Silicone Oil(4)	fair for most HC	good to 160°C
Squalane	C_2 - C_3 poor separation C_4 - C_8 acceptable separation C_9 - C_{10} peak broadening	good to only 65°C

The OV101 silicone oil column satisfied the temperature requirements for separation of C_2 to C_{10} hydrocarbons; however, only poor quantitative resolution was feasible. The squalane column did not adequately resolve C_2 to C_3 hydrocarbons (poor separation) or C_9 to C_{10} due to the peak broadening at the low temperature. Acceptable resolution was achieved for the C_4 to C_8 hydrocarbons.

In July 1974 tests were run to investigate the use of a Porasil "B" precolumn ahead of the OV101 and squalane capillary columns. Specific improvement in the resolution of C_2 to C_4 hydrocarbons was thought possible. The results of this configuration testing found that a loss of resolution developed in the C_4 to C_8 analysis and the required analysis time was excessive.

Next a dibutyl maleate column(5) 50 ft. of 1/8 inch OD copper, was fabricated for evaluation. It was believed that this configured column would resolve C_5 through C_9 hydrocarbons. Tests conducted at 0°C demonstrated poor resolution (broad peaks), hence, this column was not considered suitable for operational application.

In mid July 1974 a meeting was held with the EPA Project Officer, Rockwell's Principal Investigator and supporting staff personnel. The objectives of the meeting were twofold:

1. Review the current analysis capability of the RAPS gas chromatograph laboratory in support of the Summer 1974 Intensive and
2. Review the progress to date, problems, and establish a plan of action to bring the Perkin Elmer PE 900 Chromatograph into operational service.

At this meeting it was agreed to drop further development work aimed at the use of a single column for hydrocarbon analysis for compounds C_2 through C_{10}. Thus the capability for simultaneous analysis of two samples would no longer be feasible. One channel of the dual chromatograph was to be used for separation and analysis of the light gas compounds C_2 through C_4, and the second channel for the heavy compounds C_4 through C_{10}.

Three packed columns, Porasil B$^{(6)}$ and two Durapaks: n-octane and phenyl isocyanates,$^{(7)}$ were investigated to provide the C_2 - C_4 hydrocarbon analysis. The Porasil B column gave the best separation of the three, resolving all the C_2 - C_4 hydrocarbons of interest above 5 ppb. concentration. Figures 1, 2, and 3 illustrate the respective separation of a mixture of C_2 - C_4 hydrocarbons on each column. Reproducibility of the Porasil B analysis and trapping system was determined with a sample of auto exhaust collected in a Teflon bag. The results of this study are tabulated in Table 1, inferring the reproducibility of trapping heavy hydrocarbon to be as good or better than the light C_2's trapped in this test. Limitations involved with the Porasil B are the lack of complete resolution of C_2 compounds at high concentrations and the peak broadening of compounds whose elution time is greater than five minutes. These problems can be seen in Figure 1.

For C_4 through C_{10} hydrocarbon analysis, a squalane SCOT (Support Coated Open Tubular) capillary column was investigated. Temperature programming from 0^o to 65^o did not separate the C_2 and C_3 hydrocarbons but did minimize the bleed of the squalane liquid phase. To facilitate the C_{10} hydrocarbon resolution, an Analabs flow programmer was used to flow program (from 10 to 40 cc per minute) the column after the column temperature reached 65^oC. This configuration provided acceptable resolution of C_4 to C_8 hydrocarbons in seventy-

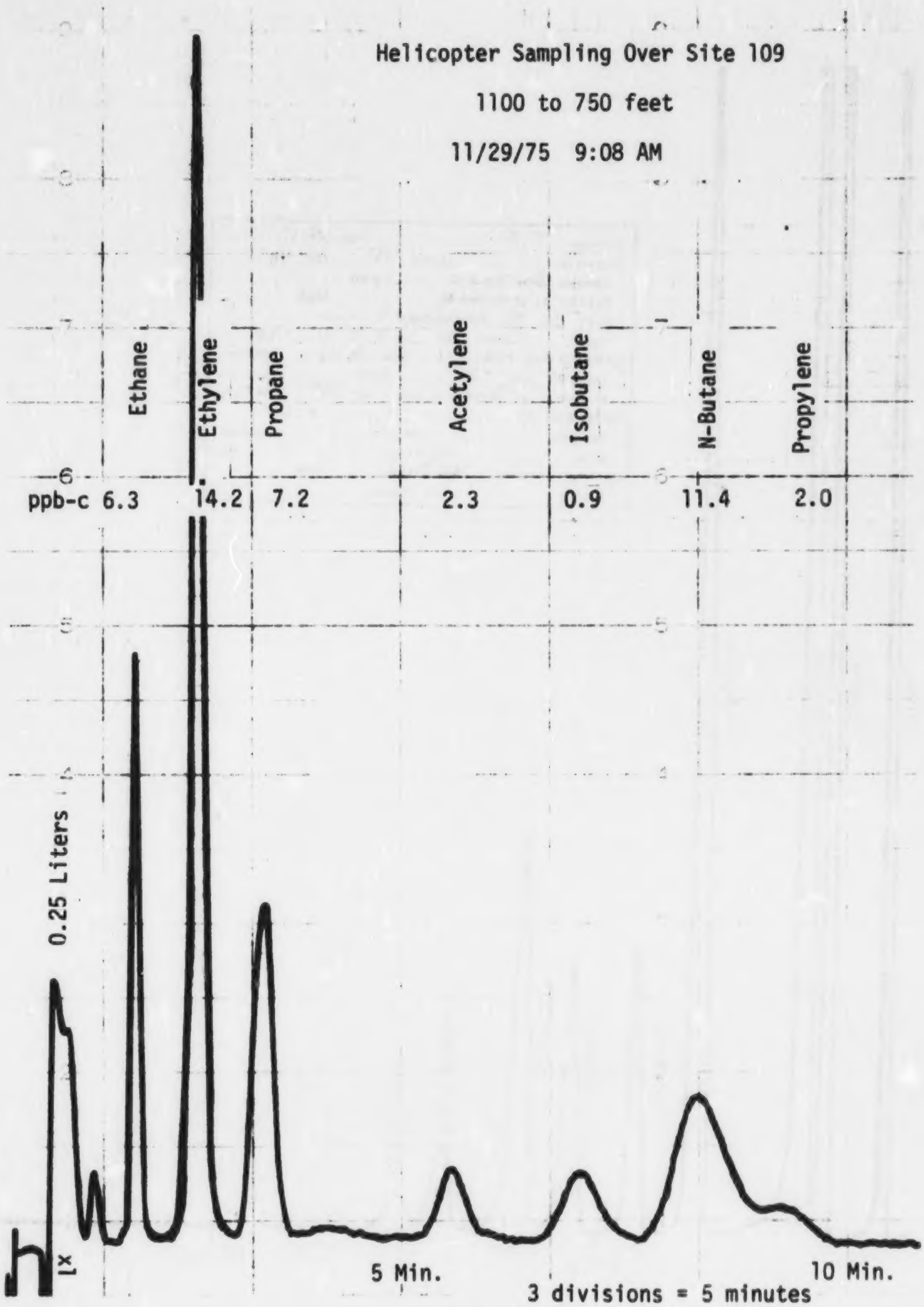
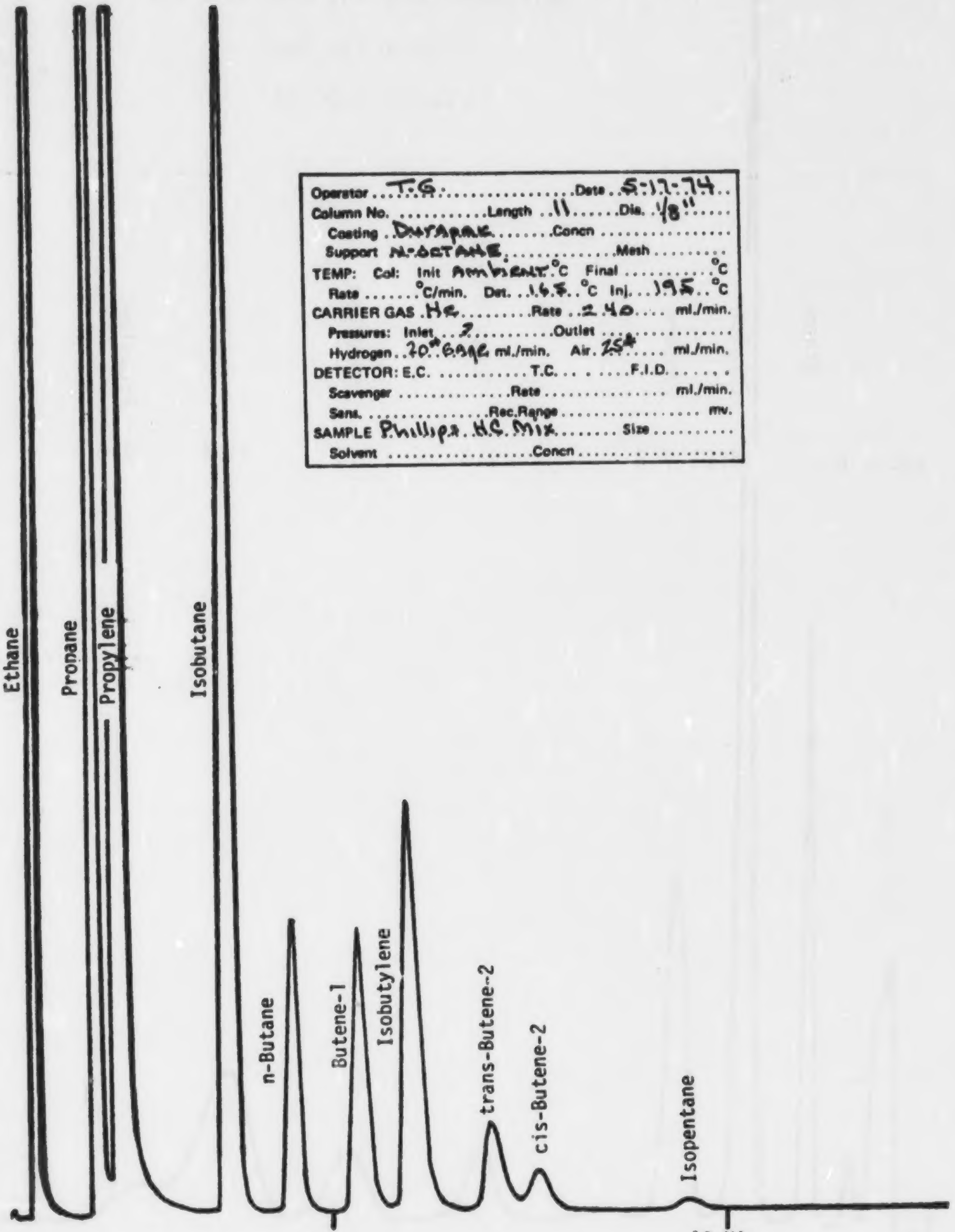


FIGURE 1

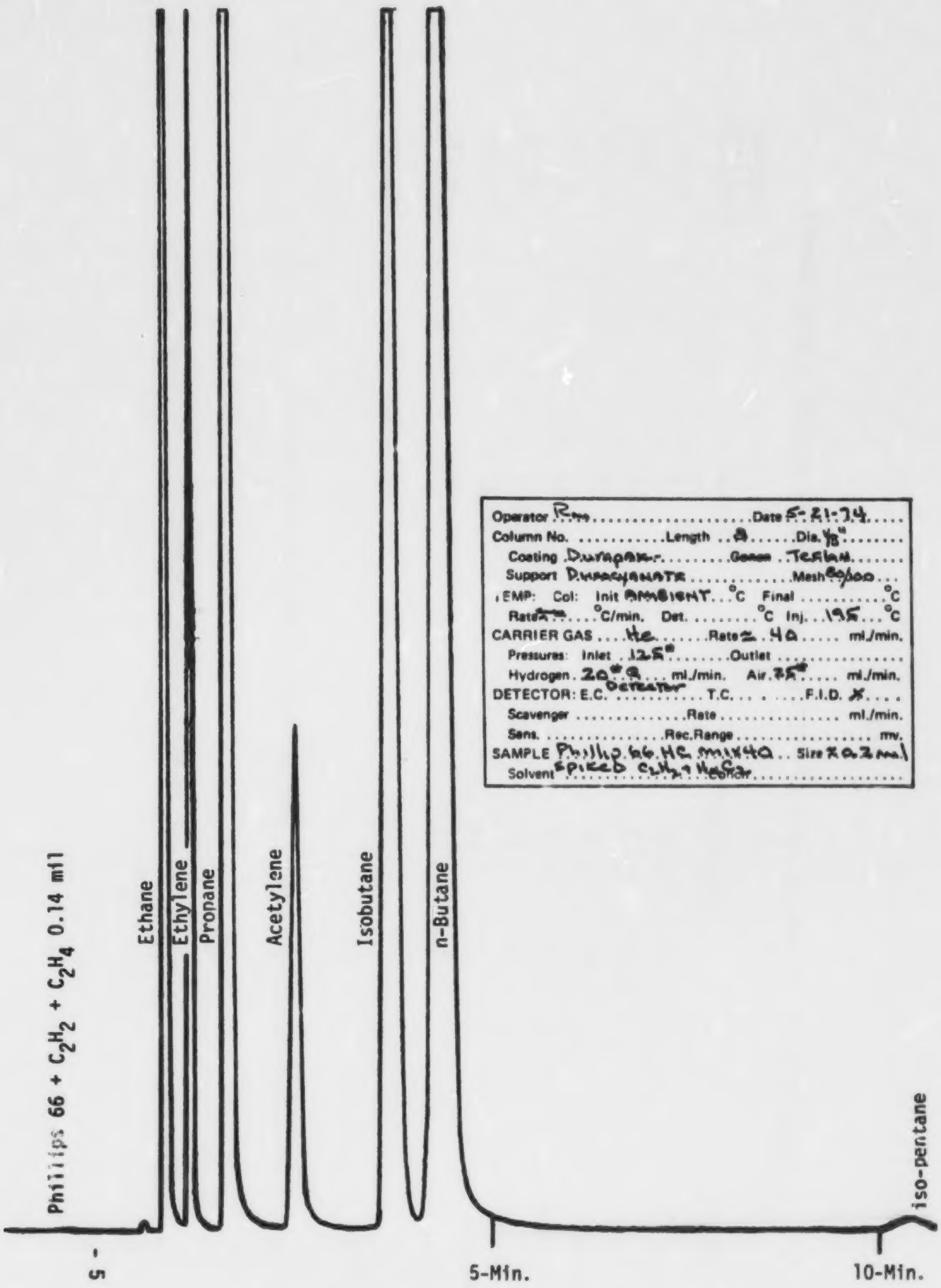
C_2 - C_4 HYDROCARBON ANALYSIS ON PORASIL B COLUMN



Operator T.G. Date 5-17-74
Column No. Length 11 Dia. 1/8"
Coating Durapak Concn
Support N-OCTANE Mesh
TEMP: Col: Init Ambient °C Final °C
Rate °C/min. Det. 165 °C Inj. 195 °C
CARRIER GAS He Rate 240 ml./min.
Pressures: Inlet 7 Outlet
Hydrogen 20# Gage ml./min. Air 25# ml./min.
DETECTOR: E.C. T.C. F.I.D.
Scavenger Rate ml./min.
Sens. Rec.Range mv.
SAMPLE Phillips HC Mix Size
Solvent Concn

FIGURE 2

C_2 - C_4 HYDROCARBON ANALYSIS ON DURAPAK N-OCTANE COLUMN



Operator R... Date 5-21-74
Column No. ... Length 8 ... Dia. 1/8"
Coating Durapak ... [illegible] Teflon
Support [illegible] ... Mesh 80/100
TEMP: Col: Init AMBIENT °C Final °C
Rate — °C/min. Det. °C Inj. 195 °C
CARRIER GAS He Rate ≈ 40 ml./min.
Pressures: Inlet 125# Outlet
Hydrogen 20#@ ml./min. Air 35# ml./min.
DETECTOR: E.C. Detector T.C. F.I.D. X
Scavenger Rate ml./min.
Sens. Rec.Range mv.
SAMPLE Phillips 66 HC mix #40 Size ≈ 0.2 ml
Solvent SPIKED C_2H_2 + H_4C_2 Concn.

FIGURE 3

C_2 - C_4 HYDROCARBON ANALYSIS ON DURAPAK PHENYL ISOCYANATE COLUMN

TABLE 1

REPRODUCIBILITY OF COMPLEX AUTO EXHAUST (72 VW) USING PE 900 GAS CHROMATOGRAPH

COMPONENTS	PEAK AREAS*			AVERAGE	STANDARD DEVIATION
Ethane	0.20	0.20	0.18	0.19	± 0.01
Ethylene	0.65	0.51	0.65	0.60	± .081
Propane	0.05	0.05	0.045	0.05	± 0.003
Acetylene	0.28	0.31	0.29	0.30	± 0.015
Isobutane	0.19	0.20	0.19	0.19	± 0.005
n-Butane	0.61	0.59	0.61	0.60	± 0.011
Propylene	0.37	0.35	0.41	0.38	± 0.031

NOTES:

A. Sample of auto exhaust was 1:3 of auto exhaust to ambient outside air.

B. Engine was cold.

C. Porasil B Column used.

* Calculated as peak ht, x peak width at half-height, inches^2.

two minutes. See Figure 4 for an example of relative retention times of C_4 - C_8 hydrocarbons. Reproducibility of the PE 900 system was determined with repetitive analyses of a site sample (105, 4-6 AM, 8/25/74). Fourteen compounds, C_3 to C_8 hydrocarbons, their peak area measured with the PEP-1 data processor, were compared and the standard deviation determined for each compound. The results of this study are contained in Table 2.

3.4.1.2 Concentration Trap Development

When the previous multi-stage concentration trap was proven ineffective, an investigation was conducted to determine the parameters that effect trapping efficiency; such as, trap material, coolant, and size. Copper was chosen over steel for heat transfer; liquid oxygen vs liquid nitrogen to minimize the oxygen build up that extinguishes the flame, and 1/4 in. OD tubing with 60/80 mesh glass beads to 1/8 in. to prevent water freezing out. Two traps were used, one to collect the sample (0.250 in. OD x 0.155 in. ID x copper, filled with 60/80 mesh glass beads) and the other (0.125 in. OD 0/065 in. ID copper, empty) to inject the sample as a slug into the analytical sample column. The dual trapping system was incorporated because of the time necessary to flush the collected sample from the glass bead trap, which does not allow quantitative introduction of the sample. Both traps were coated internally with SE 550 methyl silicone oil to prevent interaction of the sample with the active copper surface. Trapping efficiency is shown both in Table 1 and 2, relating to the analysis on the Porasil B and squalane columns.

3.4.1.3 Analysis

Routine analysis operation with the PE 900 initiated in August 1974 and continued thru completion of the Summer 1974 intensive (25 July thru 28 August 1974). During this period a total of 205 analyses were performed using this chromatograph. Of this total, 141 C_2 - C_4 analyses on Porasil B were performed on helicopter samples and bag samples collected in support of the Long Path Monitoring and Pollutant Variability Studies (Mr. Lou Chaney). Sixty-four (64) analyses were performed for C_4 - C_8 using the squalane column.

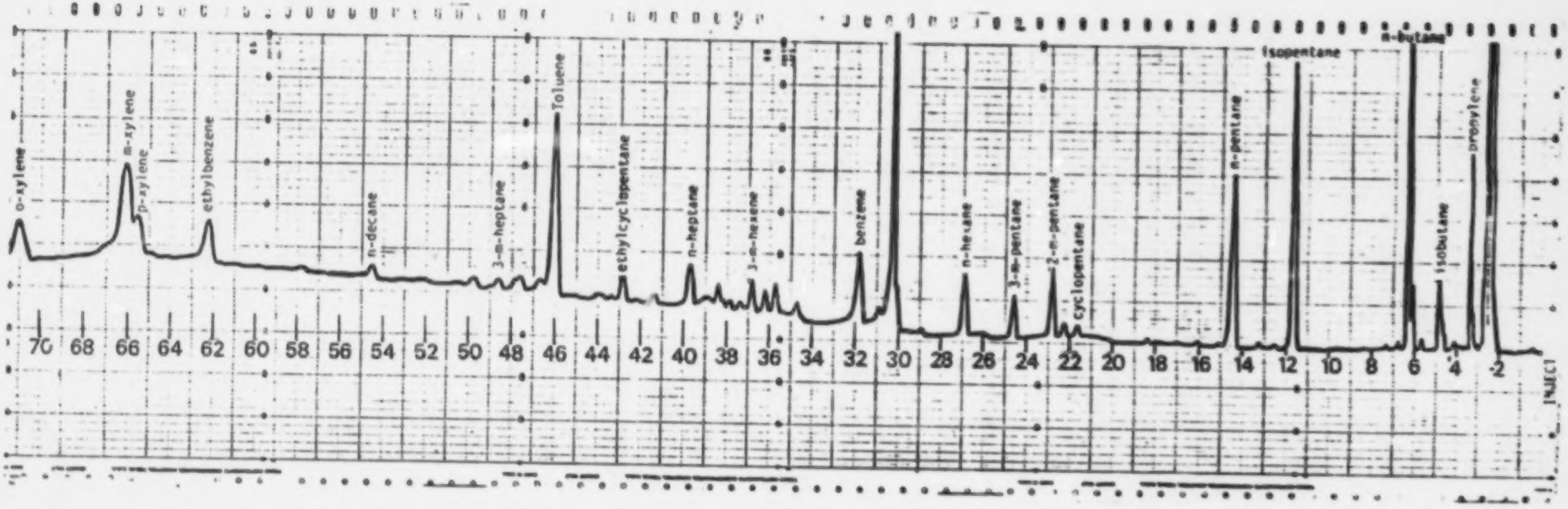


FIGURE 4 - RETENTION TIME OF C_4 - C_8 HYDROCARBONS

TABLE 2

REPRODUCIBILITY OF PE 900 ANALYSIS

8-25-74

COMPONENTS	ANALYZED 9-17		ANALYZED 9-18			ANALYZED 9-19					
	1:25 PM	3:30 PM	8AM	10:35 AM	2:40 PM	8AM	10:45 AM	1PM	3:40 PM	AVG	σ
Propane	0.366	0.258	0.435	*	*	0.235	0.247	0.221	0.336	0.300	.080
Propylene	1.663	2.516	1.762	*	*	4.338≠	2.001	1.096	1.798	1.806	.464
iso-butane	0.461	1.109	0.500	*	*	1.336	0.618	0.333	0.441	0.685	.378
isobutylene	0.337	0.201	0.243	*	*	0.195	0.216	0.314	0.321	0.261	.062
n-butane	1.914	3.177	1.994	*	*	4.530≠	2.329	1.357	1.703	2.079	.627
iso-pentane	1.599	1.581	1.505	*	*	1.631	1.218	0.999	1.177	1.387	.224
n-pentane	2.135	1.132	1.889	*	*	1.349	1.254	1.070	1.261	1.441	.406
2-methyl pentane	29.225	28.317	31.215	35.007	34.524	28.600	30.565	26.228	31.593	30.586	2.881
2-4 dimethyl pentane	5.691	6.413	5.970	6.469	6.308	8.607	6.970	6.724	7.537	6.743	0.883
Toluene	7.771	7.524	7.577	7.618	7.888	6.724	7.092	18.243	7.382	7.447	0.379
Ethyl Benzene	7.726	7.511	7.392	8.119	8.361	6.660	7.535	7.915	7.430	7.628	0.496
p-xylene	11.258	10.958	11.598	11.842	12.083	9.911	11.320	9.558	11.070	11.066	0.828
m-xylene	23.629	23.684	22.432	25.114	24.964	20.813	22.599	19.936	22.459	22.848	1.730
o-xylene	5.837	5.619	5.488	5.833	5.873	5.071	5.724	6.006	5.493	5.660	0.280

* Computer did not give area measurement

≠ Exceeds 2σ limit

During the entire period of this task order, including the summer 1974 intensive period, 82 RAMS site samples were analyzed on both the 6800 and the silica gel analysis. Squalane analysis was performed on 38 on these samples.

Following the completion of the gas analysis in support of the 1974 Summer Intensive Study, it was decided by EPA that better resolution for the C_2 - C_4 analysis was necessary and that better resolution and extension to C_{10} hydrocarbons was necessary for the heavier hydrocarbons analysis. Prior to the November 74 Intensive, the Porasil B packed column was substituted with the phenyl-isocyanate Durapak column, when the former column was found to be affected by components in the air causing peak broadening at low concentrations. Twenty-four (24) analyses of helicopter samples were performed for C_2 - C_4 hydrocarbons using the phenyl-isocyanate column during the November Intensive. No further effort was expended investigating improved column configurations due to the fact that Mr. Walker's services were discontinued, and also the requirement existed to support the forthcoming November 74 Intensive.

3.4.2 Beckman Model 6800 Chromatograph

The Model 6800 Chromatograph is designed for monitoring six air pollutants, total hydrocarbons, methane, carbon monoxide, ethane, ethylene and acetylene. It is composed of a flame ionization detector, a pressure actuated valve introduction system, and a three column analysis system.

The three columns are:

1. A prestripper column of Triton X-350 combined with silica gel for removal of H_2O, CO_2, and hydrocarbons, other than methane.
2. Molecular sieve 5A, used for the separation of methane (CH_4) and carbon monoxide (CO) after the sample elutes from the prestripper column.
3. Porapak N provides the separation of the C_2 hydrocarbons.

Total hydrocarbon analysis (THC) is directly analyzed from a sample loop into the flame detector.

Zero grade air (99.9999% purity) is supplied from certified bottled gas and is prepurified by catalytic oxidizer for use as the carrier gas in the THC analysis, C_2 analysis, and as support air for the flame detector. Hydrogen is supplied from a hydrogen generator (99.9999% purity) through a molecular sieve 5A trap for carrier gas in the CO-CH_4 analysis and as fuel for the flame detector.

3.4.2.1 Chromatograph Modification

At the time work was initiated on this task order the Beckman 6800 Chromatograph had been set up in the laboratory and was operational. This chromatograph, as normally designed, will detect hydrocarbons as low as 20 ppb. However, the RAPS requirements were to measure ethylene and acetylene in the 1 to 6 ppb range.

The sensitivity for C_2 hydrocarbons was later approximately doubled by changing the value of the input resistor on the amplifier and increasing sample loop size and/or flow rate. In this configuration, normal bag analysis required about 40 to 60 liters of sample gas for two or three CH_4, CO, THC and C_2 hydrocarbon analysis. To conserve sample gas, the excess sample gas not normally routed through the three sample loops was re-routed back to the sample bag as depicted in Figure 5.

In November, a further modification to the pumping system was incorporated by establishing the pump downstream of the sample loops and to pull the sample through rather than pump it(8). This will allow a smaller sample to be removed from the bag sample and prevent possible dilution of the sample with air from the pump.

3.4.2.2 Beckman 6800 Chromatograph Reproducibility

To determine the reproducibility of the 6800 chromatograph a Teflon bag was filled with hydrocarbon free air, CO (3.0 ppm), CH_4 (3.0 ppm), C_2H_4 (1.0 ppm), and C_2H_2 (1.0 ppm). The bags were analyzed ten times and peak heights measured. From these measurements, the standard deviation for each compound was calculated.

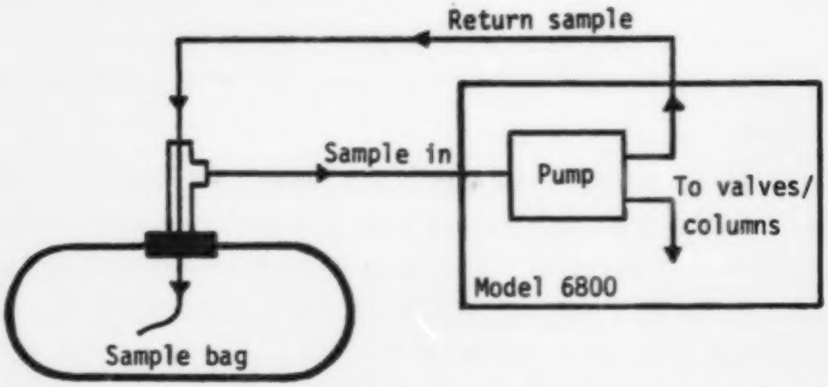

Return sample
Sample in
Pump
To valves/
columns
Model 6800
Sample bag

FIGURE 5

Beckman Model 6800 Bag Sampling System

The results are presented in Table 3. These results indicated that satisfactory reproducibility (σ = 1.5% or better) could be obtained.

3.4.2.3 Efficiency Check of Carbon Monoxide - Methane Conversion

In the analysis of carbon monoxide by the 6800 chromatograph, the carbon monoxide is catalytically converted to methane and its concentration determined as the methane response on the flame ionization detector. A comparison of equal concentrations of methane and carbon monoxide as peak area response indicated only a six percent difference, but based on peak height measurement, a 51 percent variation was found in the response.

3.4.2.4 Standard Bag Preparation and Diffusion Losses

To determine the consistency between bag standards prepared by different laboratory technicians, three different personnel prepared the same mixture of five compounds (C_2H_2, C_2H_4, CO, C_2H_6 and CH_4) in standard bags. Two technicians used 100 liter Teflon bags and the other used a 100 liter Tedlar. The results as presented in Table 4 indicate:

1. The method of bag preparation was reproducible to ± 10% between operators. Note: One exception due to operator error concerning acetylene.
2. Similar results were obtained with both Tedlar and Teflon bag materials.
3. For these materials (Tedlar and Teflon), loss via infusion or adsorption did not appear significant over twelve hours. This is assuming that significant adsorption occurs only when adsorption exceeds the ± 10% error in the preparation of standards.

It should be recognized that these results, as they relate to bag performance, are to be considered preliminary and applicable only to these test conditions. As additional experience with bags was obtained, bag history and origin were determined also to be important.

TABLE 3

STANDARD DEVIATION BECKMAN MODEL 6800

THC = Total Hydrocarbons

CO = Carbon Monoxide

C_2H_2 = Acetylene

C_2H_4 = Ethylene

N = No. of Measurement

X = Measured Values

$\bar{X}$ = Arthmetic Mean

σ = Standard Deviation

THC (10 X 2)			CO (10 X 1)		
N X (mm)	$(x - \bar{x})$	$(x - \bar{x})^2$	X (mm)	$(x - \bar{x})$	$(x - \bar{x})^2$
1 155.4	2.9	8.41	185	.5	.25
2 157.0	1.3	1.69	185	.5	.25
3 156.0	2.3	5.29	186	.5	.25
4 157.0	1.3	1.69	186	.5	.25
5 156.8	1.5	2.25	186	.5	.25
6 158.0	0.3	0.09	184	1.5	2.25
7 158.2	0.1	0.01	186	.5	.25
8 160.3	2.0	4.00	188	2.5	6.25
9 161.3	3.0	9.00	185	.5	.25
10 162.5	4.2	17.64	184	1.5	2.25
Total 1582.5		50.07	1855.0		12.50

$\sigma abs = \sqrt{\frac{50.07}{10 - 1}} = 2.36$ mm

$\sigma rel = \frac{2.36}{158.3 \times 100} = 1.49\%$ THC

$\sigma abs = \sqrt{\frac{12.50}{10 - 1}} = 1.18$ mm

$\sigma rel = \frac{1.18}{185.5 \times 100} = .63\%$ CO

C_2H_4 (10 X 1)			C_2H_2 (10 X 1)		
N X (mm)	$(x - \bar{x})$	$(x - \bar{x})^2$	X (mm)	$(x - \bar{x})$	$(x - \bar{x})^2$
1 51	0	0	88	.2	.04
2 51	0	0	88	.2	.04
3 51	0	0	83	.2	.04
4 52	1	1	87	.8	.64
5 52	1	1	87	.8	.64
6 51	0	0	89	1.2	1.44
7 50	1	1	89	1.2	1.44
8 50	1	1	87	.8	.64
9 51	0	0	88	.2	.04
10 51	0	0	87	.8	.64
Total 510.0		4	873.0		5.60

$\sigma abs = \sqrt{\frac{4}{10 - 1}} = .67$ mm

$\sigma rel = \frac{.67}{57} \times 100 = 1.31\%$ C_2H_4

$\sigma abs = \sqrt{\frac{5.6}{10 - 1}} = .79$ mm

$\sigma rel = \frac{.79}{87.8} \times 100 = .89\%$ C_2H_2

TABLE 4

STANDARD BAG PREPARATION AND DIFFUSION LOSSES

TEDLAR STD. MIX - MADE 8/28/74

Analysis of 8/28/74 5:15 PM			Analysis of 8/29/74 8:45 AM		
Component	Pk. Ht. (mm)	Conc. (ppm-c)	Component	Pk. Ht. (mm)	Conc. (ppm-c)
THC 10 x 8	202.67	8	THC 10 x 8	202.0	7.974
CH_4 10 x 2	180.33	5	CH_4 10 x 2	168.0	4.658
CO 10 x 2	127.33	5	CO 10 x 2	122.5	4.810
C_2H_4 10 x 1	66.67	1	C_2H_4 10 x 1	58.0	0.869
C_2H_6 10 x 1	93.33	1	C_2H_6 10 x 1	81.0	0.868
C_2H_2 10 x 1	109.67	1	C_2H_2 10 x 1	100.5	0.916

TEFLON STD. MIX - MADE 8/28/74

Analysis of 8/28/74 9:20 PM			Analysis of 8/29/74 9:15 AM		
Component	Pk. Ht. (mm)	Conc. (ppm-c)	Component	Pk. Ht. (mm)	Conc. (ppm-c)
THC 10 x 8	197.25	8	THC 10 x 8	192.25	7.797
CH_4 10 x 2	182.25	5	CH_4 10 x 2	177.50	4.870
CO 10 x 2	122.25	5	CO 10 x 2	118.50	4.847
C_2H_4 10 x 1	64.50	1	C_2H_4 10 x 1	61.50	0.953
C_2H_6 10 x 1	86.50	1	C_2H_6 10 x 1	84.00	0.971
C_2H_2 10 x 1	113.00	1	C_2H_2 10 x 1	99.50	0.881

TEFLON STD. MIX - MADE 8/29/74

Analysis of 8/29/74 2:45 PM			Analysis of 8/30/74 10:00 AM		
Component	Pk. Ht. (mm)	Conc. (ppm-c)	Component	Pk. Ht. (mm)	Conc. (ppm-c)
THC 10 x 8	207.25	8	THC 10 x 8	201.00	7.759
CH_4 10 x 2	194.00	5	CH_4 10 x 2	189.00	4.871
CO 10 x 2	134.50	5	CO 10 x 2	131.00	4.870
C_2H_4 10 x 1	74.50	1	C_2H_4 10 x 1	73.00	0.980
C_2H_6 10 x 1	87.50	1	C_2H_6 10 x 1	86.00	0.983
C_2H_2 10 x 1	89.00	1	C_2H_2 10 x 1	87.00	0.978

SUMMARY

STD PREP REPRODUCIBILITY

Average THC = 202.39 ± 5 mm, ± 2.47%
Average CH_4 = 184.53 ± 7.4 mm, ± 4.0%
Average CO = 128.03 ± 6.2 mm, ± 4.8%
Average C_2H_4 = 68.56 ± 5.2 mm, ± 7.7%
Average C_2H_6 = 89.11 ± 3.2 mm, ± 4.1%
Average C_2H_2 = 103.89 ± 13 mm, ± 12.5%

ADSORPTION REPRODUCIBILITY

	ΔC (%)	σ(%)
Average THC	- 1.9	1.4
Average CH_4	- 4.0	2.4
Average CO	- 3.2	0.6
Average C_2H_4	- 6.6	5.7
Average C_2H_6	- 5.9	6.3
Average C_2H_2	- 7.5	4.9

Note

Beckman 6800 Chromatograph Was Used.

3.4.2.5 Calibration of Instruments

The standards for the Beckman 6800 were synthetic standards consisting of CO and CH_4 at approximate ambient concentrations (i.e. CH_4 = 4 ppm and CO = 2 ppm). Any deviation from these concentrations for an unknown gas sample could be calculated using the fact that the unknown concentration is directly proportional to its peak height. These standards were prepared on the day of the analysis.

The standards for the P-E 900 were prepared weekly. The gases involved were eight different hydrocarbons spread out over the entire C_2 to C_8 range. The unknown samples were calculated from the fact that the area of the peak is directly proportional to its concentration.

All above standards were prepared in a Teflon bag filled with a known amount of Linde zero air. Precision syringes were used to inject known amounts of standard gases from their respective tanks of pure known gases.

3.4.2.6 Analysis

During the period of performance on this task order, the Beckman 6800 Chromatograph analyzed 201 gas samples collected from the RAMS network, RAPS helicopters, Winnebago mobile laboratory, portable samplers and various special samples.

3.4.3 Varian, Model 940 Gas Chromatograph

Analysis of halogenated compounds of SF_6 fluorocarbons 11 and 12 were to be performed in the gas chromatograph laboratory using a Varian, Model 940 gas chromatograph. This instrument was received in late August minus the detector. Application for license from the Atomic Energy Commission (AEC) had been applied for previously in July for the isotope detector. After the license was granted in September, the detector was received and installed. Two columns were prepared for analysis of SF_6 and fluorocarbons. Due to other higher priority effort, no further effort was expended on this instrument during the remaining period of this task order.

3.4.4 Bendix, Model 8101-B, NO_X Analyzer

This instrument was received late in October 1974. No effort was expended setting the analyzer up for use during the period of performance of this task order.

3.4.5 Tracor, Model 270, Sulfur Chromatograph

The determination of total sulfur, sulfur dioxide, hydrogen sulfide and methyl mercaptan in air samples were to be made using a Tracor, Model 270, Sulfur Chromatograph. This instrument was received in August 1974 and set up by the manufacturer's field representative. Initial checkout and testing found a suspected bad analytical column which was returned to the factory for replacement. The problem was found to lie in the temperature setting of the analysis column and in October the chromatograph was placed back in operation and calibrated. Figure 6 depicts the relationship of response for concentrations of 45 to 180 ppb of SO_2 in air.

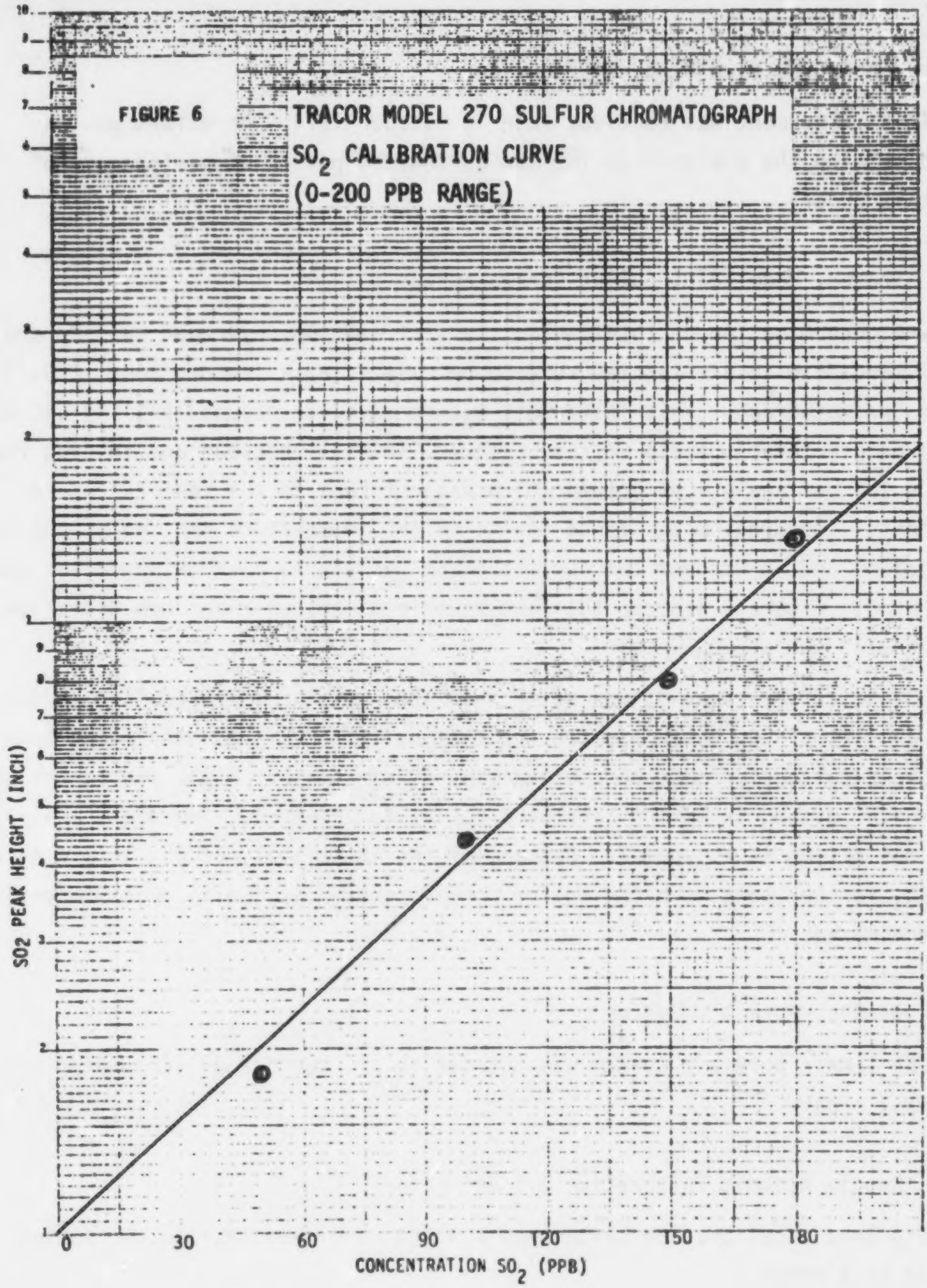
During calibration, it was noted that there was some degradation in the reproducibility of SO_2 data. Subsequent testing revealed that the Teflon bags used for sample collection must be preconditioned before use. Also, due to the short "half-life" of SO_2 in Teflon bags used for sulfur analysis, immediate analysis after collection is essential. Because of the instability of SO_2 in a gas sample bag, further work with the sulfur chromatograph for the November Intensive was terminated.

3.4.6 Bendix, Pure Air System

The Bendix pure air system was not set up or used during the period of this task order.

3.4.7 Bendix Dynamic Calibration System

The Bendix calibration system was not set up or used during the period of this task order.



4.0 SAMPLE BAG ANALYSIS AND TESTING

Operation and use of the RAMS gas bag collection system was initiated in April 1974. Analysis of these early samples found that there was significant bag contamination over and above the "total hydrocarbon" as measured by the Beckman 6800 Chromatograph in the RAMS station. To alleviate this problem, investigations into methods of bag decontamination were studied.

4.1 BAG CLEANING

Initial bag cleaning methods studied were by the use of heating and vacuum. Four new bags, 2 Teflon and 2 Tedlar, were "polluted" with a standard mixture of 6 ppm and C_1 - C_{10} hydrocarbons. Two bags, one Teflon "A" and one Tedlar "B" were placed in a 65^0 oven with their inlets open for 60 minutes. After removal from the oven and cooling, the bags were filled with HC free air, and their total hydrocarbons immediately measured. Bag "A" contained 4.5 ppm THC and bag "B" 4.3 ppm THC. Next the vacuum cleaning test was run. The remaining two bags (Teflon, bag "C" and Tedlar, bag "D") were held at vacuum for fifteen minutes. The bags were then filled with hydrocarbon free air after vacuum treatment and immediately analyzed. Bag "C" measured 0.15 THC and bag "D" 0.20 ppm THC. From these results it was decided to use the vacuum method for bag cleaning in the future. All new and used bags were cleaned by this procedure before use and sample collection.

4.2 BAG LEAK TESTING

From the initiation of bag sample collection and analysis, the major problems experienced were with leaking sample bags. New bags as well as used bags were found to leak. To minimize the loss of samples, all bags were given a leak test prior to use and installation in a RAMS station. New bags found to leak were returned to the supplier for repairs or replacement and used bags were resealed (when possible) and leak tested before they were placed into service.

Leak testing consisted of filling each 100 liter bag with approximately 80 liters of air. The bag was next left to sit for 24 hours, preloaded by placing a book (about 1 lb.) on top. If there was less than a 10% loss of air, the bag was considered suitable for service.

4.3 BAG CONTAMINATION TESTING

In August 1974 tests were performed to investigate diffusion losses through bags. Three standard bag samples were prepared, two in Teflon bags and one in Tedlar. Analysis was performed on each bag immediately after preparation and again the next day. The results are shown in Table 4. Additional experiments dealing with bag material losses were performed and the results are shown graphically in Figures 7 and 8.

In October 1974 a test was conducted to investigate variation of hydrocarbon concentration with time in Tedlar bags. New Tedlar bags (36 x 40 inches) were made up, leak tested and cleaned. A Scott standard blend used for this investigation was compared with a laboratory prepared standard to determine each component concentration. The test was initiated with duplicate bags on 23 October and analyzed periodically through October. The result of this bag test is presented in Table 5. In general, with the exception of THC, no significant changes in concentration were found after sixty-nine hours. The indicated loss of C_2 hydrocarbons in bag "A" late in the test was due to depletion of the sample.

DECAY OF SELECTED MATERIALS THROUGH A 5 MIL TEFLON BAG

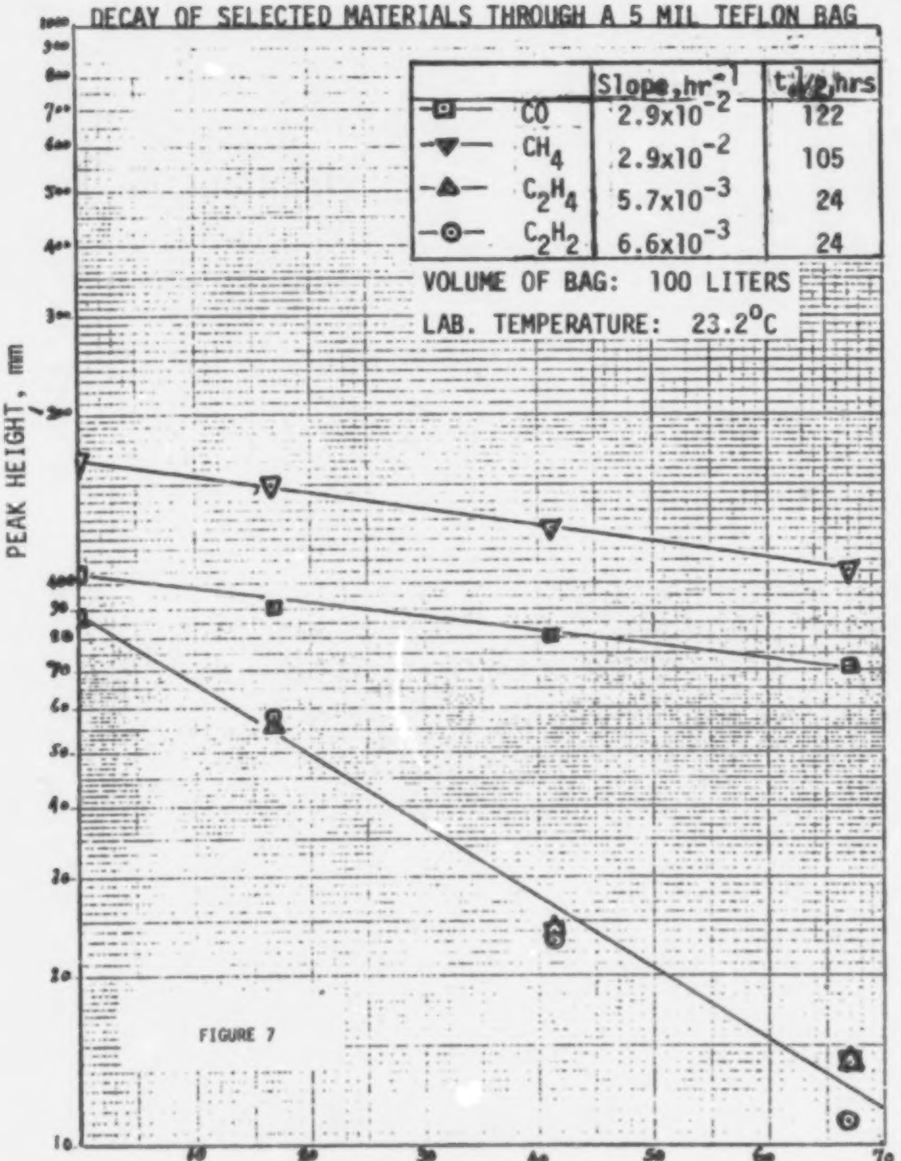
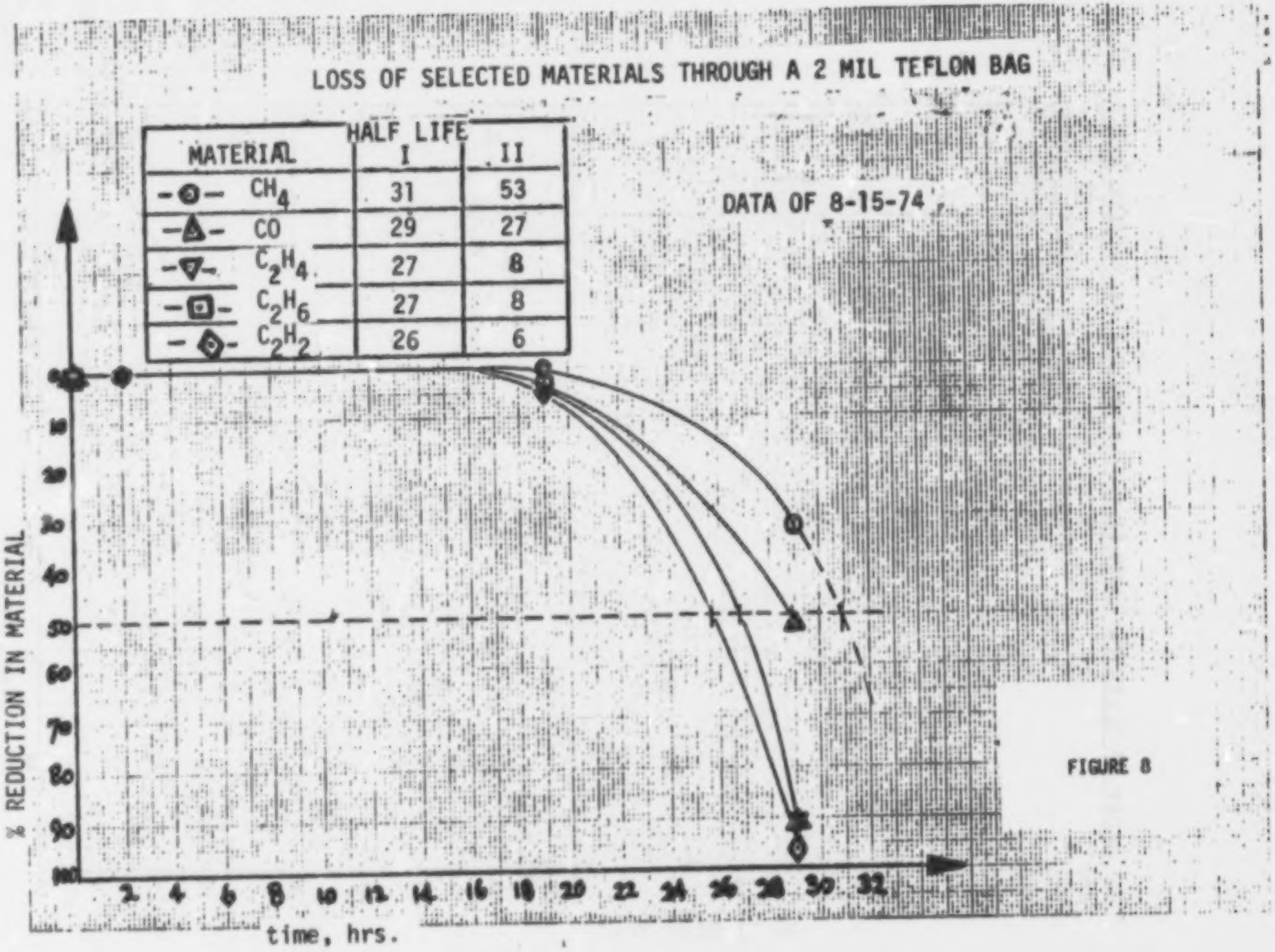


FIGURE 7

LOSS OF SELECTED MATERIALS THROUGH A 2 MIL TEFLON BAG



MATERIAL	HALF LIFE I	II
-⊙- CH_4	31	53
-△- CO	29	27
-▽- C_2H_4	27	8
-⊡- C_2H_6	27	8
-◇- C_2H_2	26	6

FIGURE 8

TABLE 5

HYDROCARBON RETENTION TEST USING TEDLAR BAG MATERIALS

Sample	Time (hours)	Total Hydrocarbons	Methane (ppm)	Carbon Monoxide (ppm)	Ethylene (ppm)	Ethane (ppm)	Acetylene (ppm)
Bag A	0	1.96	1.83	3.71	0.444	0.423	0.300
	2.25	2.02	1.79	3.43	0.441	0.430	0.302
	5.33	2.04	1.79	3.51	0.448	0.424	0.201
	22.50	2.22	1.81	3.60	0.456	0.432	0.307
	26.00	2.11	1.77	3.54	0.456	0.439	0.313
	45.75	2.14	1.74	3.68	0.442	0.426	0.298
	54.00	2.46	1.74	3.63	0.436	0.420	0.290
	69.75	2.59	1.71	3.55	0.350	0.333	0.232
	0.50	1.83	1.73	3.51	0.444	0.428	0.303
	2.85	1.88	1.78	3.45	0.451	0.423	0.304
	5.00	1.89	1.77	3.45	0.448	0.429	0.304
	22.00	2.04	1.79	3.57	0.460	0.440	0.313
	26.50	2.03	1.81	3.57	0.456	0.440	0.311
	45.00	1.88	1.74	3.63	0.442	0.429	0.300
Bag B	54.50	2.28	1.74	3.68	0.447	0.428	0.298
	69.00	2.26	1.73	3.65	0.436	0.416	0.292
	93.00	2.37	2.12	4.34	0.486	0.464	0.317
Concentration of Scott Standard Blend							
Analyzed	10-21	1.631	1.756	3.737	0.490	0.453	0.320
	10-29	2.070	1.830	3.630	0.482	0.482	0.348
Average		1.850	1.790	3.683	0.486	0.486	0.334

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PART III: DEVELOPMENT OF METHODS

AND

ANALYSES OF ATMOSPHERIC POLLUTANTS

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1.0 INTRODUCTION

The St. Louis Regional Air Pollution Study is being conducted to develop, evaluate and validate air-quality simulation models for both urban and rural areas of stationary and mobile pollution sources. The RAPS Gas Chromatography Laboratory supports a variety of studies under the program; e.g.

A. Evaluation of the Regional Air Monitoring Stations (RAMS) sites.

B. Validation of Automotive Emissions Inventory Submodels.

C. Defining the composition of emissions from significant sources.

D. Tracking plumes.

E. Developing and Validating Photochemical Submodels.

The objective of this Task Order was to provide support of the various RAPS programs through the development of methods and analyses of atmospheric pollutants. Data from all analyses are recorded and entered into the RAMS/RAPS Data Computer Bank.

2.0 TASK ORDER REQUIREMENTS

Under the Task Order the contractor was to provide the necessary manpower, materials and services to perform the following:

2.1 SERVICES

2.1.1 Work Plan

The contractor shall prepare and submit for approval to the RAPS Field Coordinator a work plan for operation of the Gas Chromatography Laboratory. The plan shall include schedules, manpower estimates, and milestones for bringing the Gas Chromatography Lab operational for analysis of atmospheric samples. The work plan shall include quality control, sample handling, operation and calibration procedures for all government furnished (GFE) instruments. It shall also include procedures for entry and retrieval of data (into/from) the RAMS/RAPS data bank.

2.1.2 Methodology

The contractor shall establish and conduct analyses for C_1 - C_{10} hydrocarbons, CO, total hydrocarbons, NO_x, total sulfur, SO_2, H_2S, CH_3SH, and atmospheric tracer gases, such as SF_6, and fluorocarbons 11 and 12. Except for methane, hydrocarbons must be measured at concentrations down to one part per billion carbon (ppb C), CO to 0.01 ppm, sulfur compounds to 0.1 ppb, and tracer gases to 1 pp trillion. Measurements shall also be made for total sulfur and NO_x at atmospheric levels.

2.1.3 Sampling

Sampling shall be conducted at the RAMS monitoring stations from helicopters, from mobile vehicles, and at various sites in the St. Louis area. The contractor shall pick up and deliver to the Gas Chromatography Lab all bag samples collected at the RAMS stations. The bags shall be shielded from sunlight during pick-up and delivery. The contractor shall replace filled bags at the RAMS stations with clean, leak-tight bags.

2.1.4 Special Analysis

The contractor shall concentrate and analyze atmospheric samples for specific experiments conducted by RAPS investigators.

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2.1.5 Routine Analysis

The contractor shall analyze about 700 atmospheric samples for individual hydrocarbon (C_1 - C_{10} inclusive), total non-methane hydrocarbons (NMHC), CO and NO_X, and total sulfur, H_2S, SO_2 and CH_3SH, and for atmospheric tracer gases (SF_6, fluorocarbons 11 and 12).

2.1.6 Analysis Reports

The contractor shall validate all analyses, record and report concentrations for all chemical species specified above as well as sum of paraffins less methane, sum of olefins, and sum of aromatics.

2.1.7 Laboratory Operation

The contractor shall operate all laboratory equipment, perform instrument calibrations, routine service and maintenance. EPA will provide necessary replacement of major parts and emergency services normally performed by instrument manufacturers for all GFE instruments.

2.1.8 Administration

The contractor shall provide all necessary administrative and operational support for contract personnel assigned to this task.

2.1.9 Reports of Work

The contractor shall provide each month a technical and financial progress report.

2.2 PERSONNEL

The contractor is to provide the following personnel as a minimum:

a. One gas chromatographer.

b. One laboratory technician experienced in quantitative analysis of gases.

c. Part-time laboratory assistant for sample collection.

2.3 EQUIPMENT

The contractor shall furnish all necessary equipment and supplies required for efficient and effective operation of the Gas Chromatography Laboratory.

2.4 PERIOD OF PERFORMANCE

Start: 1 December 1974
Completion: 15 August 1975

3.0 WORK PERFORMED

During the Task Order period, the Gas Chromatography Laboratory continued to develop methods and analyze atmospheric samples per the work plan in Appendix I. Sampling was initiated at five of the RAMS sites, predetermined by the RAPS Field Coordinator, on 2 December with collection of two samples per site, five sites per day, at three day intervals. During January the number of RAMS sites sampled was increased to seven to insure a minimum of ten samples of acceptable volume for analysis. In February, the sampling of the RAMS sites was coordinated with hi-vol filter collection at six sites per sampling day. This schedule was adhered to except for the intervals of 9 to 19 March, 1 to 9 May, and 14 June through 14 July, when time was spent correcting problems in the C_2 - C_{10} hydrocarbon analysis. Table 1 contains the Gas Chromatography Laboratory's performance record during the Task Order period, subdivided to illustrate the number of specific analyses per sample.

All analyses from the task order inception to 28 February 1975 have been tabulated and given to EPA on magnetic tape. Analyses from 3 March 1975 to 9 March 1975 have been tabulated, but not key punched pending approval of data by the Project Monitor. Analyses from 22 March 1975 to 14 June 1975 have been tabulated and given to EPA on magnetic tape. The remaining task order data from 9 July 1975 to 15 August 1975 have been tabulated and are awaiting data processing instruction from EPA.

With the acquisition of the second laboratory technician, G. Seeger, in January, the remaining instruments in the laboratory were established operational; e.g. Bendix NOX Analyzer, Tracor 270 Sulfur Chromatograph, Bendix Pure Air and Dynamic Calibration System. The work performed on each of these analyzers during the period of this Task Order follows:

3.1 PERKIN ELMER, MODEL 900B GAS CHROMATOGRAPH

This high resolution gas chromatograph was used in conjunction with a concentration system of liquid oxygen and two chromatographic columns to determine C_2 - C_{10} hydrocarbon concentrations to one part per billion. The C_2 - C_5 hydrocarbons are determined with a silica gel packed column, while the C_4 - C_{10} hydrocarbon analyses is achieved with a squalane SCOT (support coated open tubular) capillary column.

3.1.1 New Sampling System

On 11 December, W. Lonneman, EPA Senior Chemist, arrived in St. Louis to assist in establishing a column system to achieve the separation of C_2 - C_{10} hydrocarbons. A new sample concentration and injection system was incorporated, allowing backflushing of the sample trap between sampling. Figure 1 contains a diagram of the sampling system, depicting the concentration of the sample and the injection of the sample onto the chromatographic column.

TABLE 1 - GAS CHROMATOGRAPHY LABORATORY PERFORMANCE

FROM 2 DECEMBER - 15 AUGUST

Type of Sample		Max. Number Samples Possible	# Samples Collected	Number of Samples Analyzed/Analysis							Status of Sample Data		
				Total	NO_x	CO	CH_4	THC	Silica Gel	Squalane	Tabulated for Key Punch	In Key Punching	Stored Raps Data Bank
101	1	10	10	5	1	5	5	5	5		5	5	
	2	10	10	6	0	6	6	6	6		6	6	
	H												
102	1	13	13	6	2	6	6	6	6	1	6	5	
	2	20	20	10	8	10	10	10	10	4	10	3	
	H	7	7	7	6	6	7	7	7		7	7	
103	1	53	50	36	28	36	36	36	29	1	36	35	
	2	59	58	39	33	39	39	39	31	8	39	31	
	H	19	19	19	14	19	19	19	14		19	16	
104	1	10	10	8	1	8	8	8	8		8	8	
	2	10	10	4	1	4	4	4	4		4	4	
	H	--	--										
105	1	32	32	26	18	26	26	26	23	1	26	25	
	2	39	38	28	23	28	28	28	25	5	28	25	
	H	5	5	5	5	5	5	5	5		5	5	
106	1	8	8	8	6	8	8	8	8		8	8	
	2	8	8	7	6	6	6	6	6		7	7	
	H	8	8	7	8	8	8	8	8		7	7	
107	1	10	10	8	1	8	8	8	8		8	8	
	2	10	10	6	1	6	6	6	6		6	6	
	H	--	--	--									
108	1	6	5	4	0	4	4	4	4		4	4	
	2	6	5	5	0	5	5	5	5		5	5	
	H	5	5	5	5	5	5	5	5		5	0	
109	1	6	6	3	0	3	3	3	3		3	3	
	2	6	6	2	0	2	2	2	2		2	2	
	H	5	5	5	1	5	5	5	5		5	5	

TABLE 1 (Cont'd)

Type of Sample		Max.Number Samples Possible	#Samples Collected	Number of Samples Analyzed/Analysis							Status of Sample Data		
				Total	NO_x	CO	CH_4	THC	Silica Gel	Squalane	Tabulated for Key Punch	In Key Punching	Stored Baps Data Bank
111	1	12	12	11	11	11	11	11	7		11	11	
	2	12	12	7	4	7	7	7	4		7	7	
	4	--	--	--									
112	1	12	8	8	8	8	8	8	6		8	8	
	2	12	9	7	7	7	8	7	5		7	7	
	H	--	--	--									
113	1	13	13	10	3	10	10	10	10	3	10	9	
	2	20	19	16	9	16	16	16	16	7	16	10	
	H	4	4	4	4	4	4	4	4		4	3	
114	1	17	17	12	11	12	12	12	7	2	12	7	
	2	24	24	11	11	11	11	11	9	5	11	10	
	H	2	2	2	1	2	2	2	1		2	2	
115	1	21	21	20	10	20	20	20	16	3	20	18	
	2	26	26	24	20	24	24	24	17	12	24	17	
	H	12	12	12	2	12	12	12	9		12	12	
116	1	6	5	5		5	5	5	5		5	5	
	2	6	5	4		4	4	4	4		4	4	
	H	--	--	--									
118	1	10	10	8	8	8	8	8	8		8	8	
	2	10	10	8	8	8	8	8	8		8	8	
	H	4	4	4	3	4	4	4	2		4	4	
119	1												
	2												
	H	3	3	3	2	3	3	3	3		3	3	
120	1	12	10	8	8	8	8	8	6		8	8	
	2	12	9	6	6	6	6	6	5		6	6	
	H	2	2	2	2	2	2	2	2		2	2	

TABLE I (Cont'd)

Type of Sample		Max. Number Samples Possible	#Samples Collected	Number of Samples Analyzed/Analysis							Status of Sample Data		
				Total	NO_x	CO	CH_4	THC	Silica Gel	Squalane	Tabulated for Key Punch	In Key Punching	Stored RAPS Data Bank
121	1	16	16	10	10	10	10	10	6	4	10	8	
	2	22	19	12	11	12	12	12	7	6	12	7	
	H	5	5	5	4	5	5	5	4		5	4	
122	1	26	26	16	15	16	16	16	13	1	16	16	
	2	33	33	31	30	31	31	31	30	11	31	24	
	4	--	--	--									
123	1	3	3	0	0	0	0	0	0	0	0	0	
	2	10	10	7	7	7	7	7	7	7	7	7	
	H	--	--	--									
124	1	26	26	21	20	21	21	21	14	2	21	20	
	2	32	31	22	21	22	22	22	19	6	22	15	
	H	--	--	--									
125	1	12	12	7	7	7	7	7	5		7	7	
	2	12	12	9	9	9	9	9	7		9	9	
	H	--	--	--									
Other Helicopter Samples		51	51	51	24	51	51	51	51		51	24	
L.Chaney		16	16	16	--	16	16	16	--		16	13	
QC Ck.		27	27	27		27	27	27			--	--	
Griscom		3	3	3		3	3	3	3	3	--	--	
Total		911	885	688	463	688	688	688	533	50	688	564	

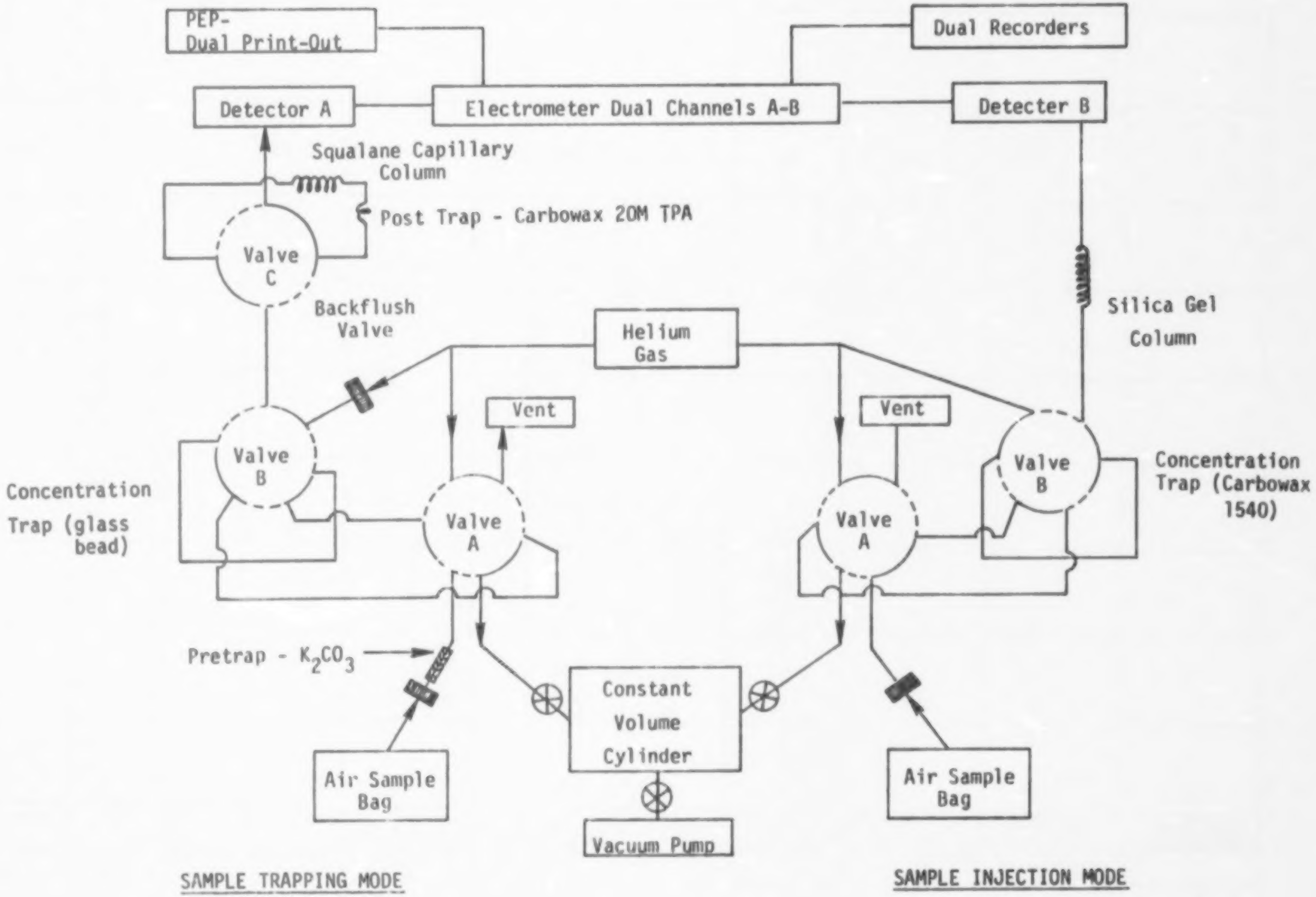

PEP-
Dual Print-Out
Dual Recorders
Detector A
Electrometer Dual Channels A-B
Detecter B
Squalane Capillary Column
Post Trap - Carbowax 20M TPA
Valve C
Backflush Valve
Helium Gas
Silica Gel Column
Vent
Vent
Valve B
Valve A
Valve A
Valve B
Concentration Trap (glass bead)
Concentration Trap (Carbowax 1540)
Pretrap - K_2CO_3
Constant Volume Cylinder
Air Sample Bag
Air Sample Bag
Vacuum Pump
SAMPLE TRAPPING MODE
SAMPLE INJECTION MODE

FIGURE 1 - ATMOSPHERIC ORGANIC ANALYSIS SYSTEM - PE900

3.1.2 C_2 to C_5 Hydrocarbon Analysis

The C_2 - C_5 hydrocarbon analysis was established with a silica gel column (3ft x 1/8 in. OD). Figure 2 contains a typical analysis of an air sample from a road sample collected 18 August using the silica gel column. In conjunction with this analysis, the PEP-1 integration system was incorporated with average response factors and individual components reported to the part per billion. The silica gel analysis was conducted on atmospheric bag samples from 12 December through the completion of the task order. The exception was during 1 April to 27 May when methane contamination in the hydrogen fuel caused erratic conditions in the analysis and prevented quantitations of the C_2 hydrocarbons.

3.1.3 C_4 to C_{10} Hydrocarbon Analysis

The C4 to C10 hydrocarbon analysis was to be conducted on a 200 foot squalane SCOT capillary column. During W. Lonneman's visit in December, it was recommended to condition the column above 100°C for a week to minimize the column bleed and conduct the analyses to 80°. After the conditioning period, the squalane column was found to have excessive column bleed for use in the C_4 to C_{10} hydrocarbon analysis. During the period of 9 to 19 March, sampling at the RAMS sites was discontinued to permit the investigation of a post column to collect the column bleed. A packed column (10 x 1/16 inch) carbowax 20M-TPA (polyethylene glycol-terephthalic acid ester) on Chromosorb W-AW was found acceptable with limited loss of resolution on the squalane column. Because of the problems in the silica gel analysis, the squalane analysis was not pursued until after W. Lonneman's visit on 5 June 1975. On his recommendation, the squalane column was reduced to 100 feet in length and the analysis limited to 75° with the post column incorporated. He also recommended the use of a pretrap of potassium carbonate (K_2CO_3) inserted prior to the concentration trap to minimize the effect of water and polar compounds with the squalane column. Figure 1 depicts the position of both the pre and post traps in the squalane system. Figure 3 illustrates a typical C_2 to C_{10} hydrocarbon analysis of an atmospheric bag sample collected from RAMS site 121 in urban St. Louis.

3.1.4 Reproducibility Study of PE900 Chromatograph

To establish the reliability of the sampling system, a roadside sample was analyzed six times over an eight hour period and the standard deviation determined for the area response of seventeen hydrocarbons found in the sample. Tabulated in Table 2 are the results of this investigation illustrating seventeen hydrocarbons ranging from C_2 to C_9 carbon number.

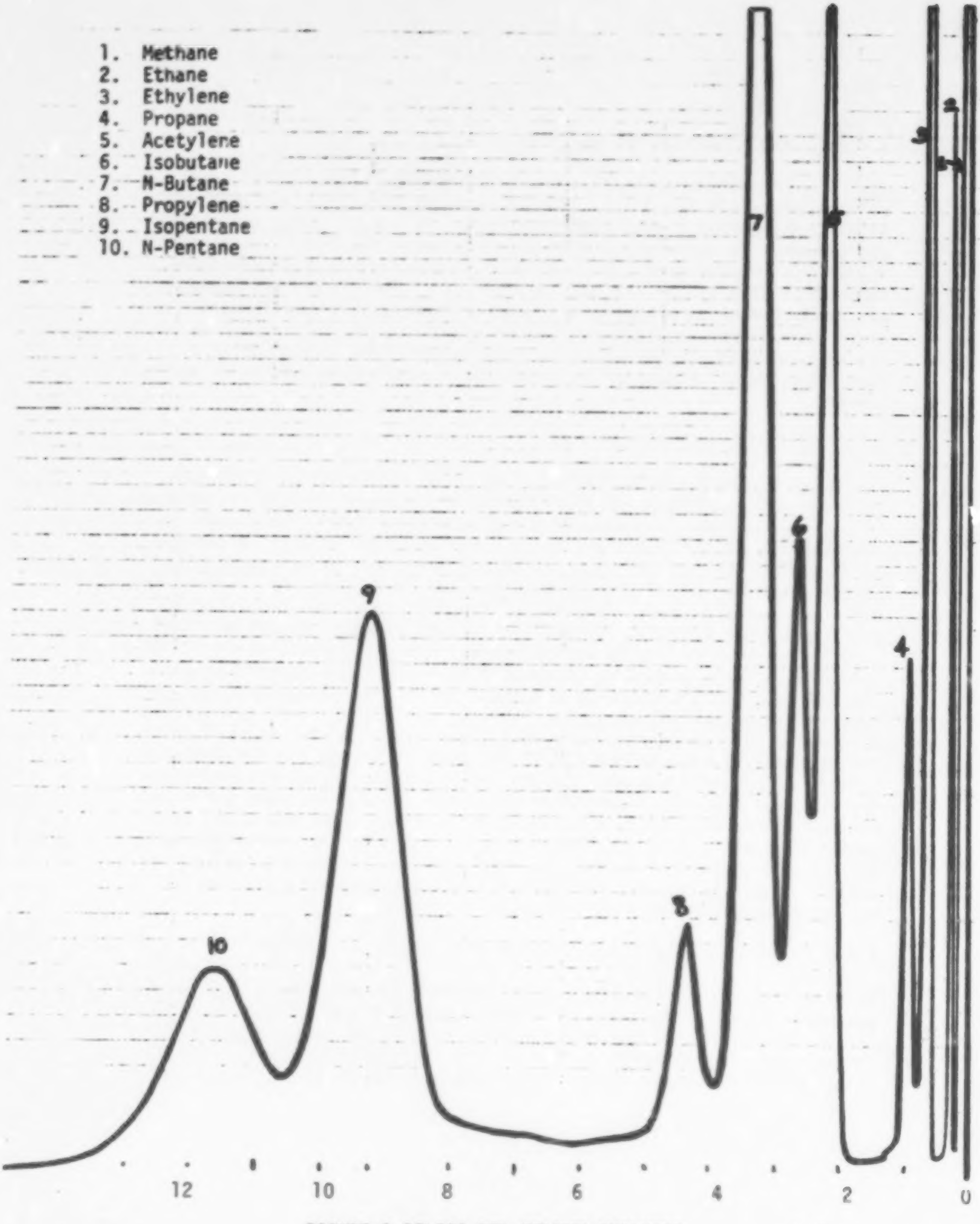


FIGURE 2 SILICA GEL COLUMN ANALYSIS
OF ATMOSPHERIC SAMPLE FOR C_2 - C_5 HYDROCARBONS

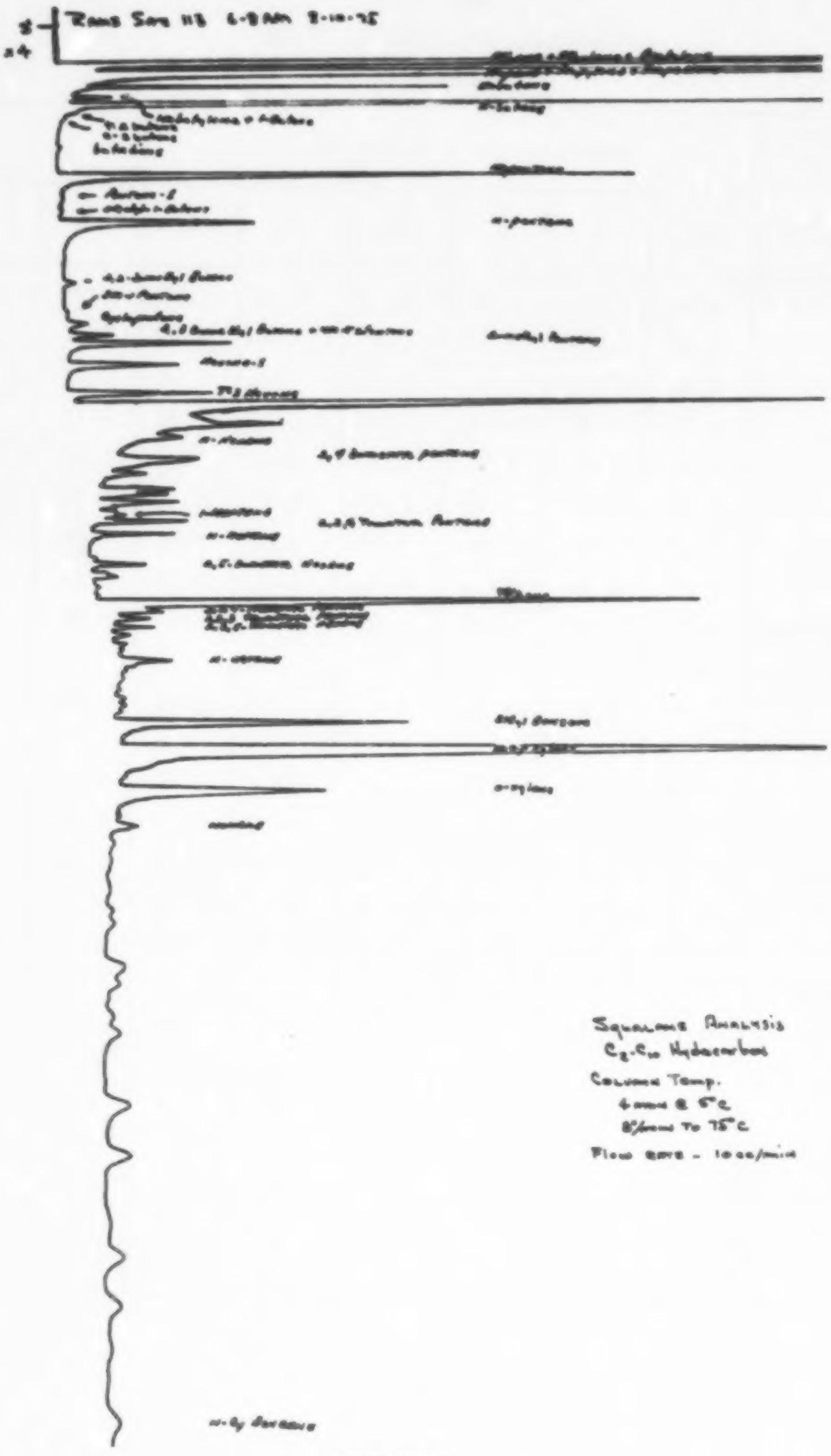


FIGURE 3

SQUALANE COLUMN ANALYSIS OF ATMOSPHERIC SAMPLE FOR C_2 - C_{10} HYDROCARBONS

TABLE 2
REPRODUCIBILITY STUDY OF PE900 CHROMATOGRAPH

Components	Analysis (Area Response)							
	1	2	3	4	5	6	$\bar{X}$	S_x
Ethane	4.80	4.73	4.60	4.60	4.80	5.18	4.79	0.21
Acetylene	2.74	2.65	2.67	2.70	2.65	2.85	2.71	.08
Propylene	1.10	1.09	1.13	1.13	1.16	1.16	1.13	.03
n-Propane	2.71	2.70	2.68	2.69	2.73	2.88	2.73	.07
Isobutane	1.94	1.93	1.95	2.00	2.00	2.04	1.98	.04
n-Butane	6.36	6.39	6.38	6.43	6.42	6.80	6.46	.17
Isopentane	7.06	6.96	6.96	7.04	7.03	7.46	7.09	.19
n-Pentane	5.28	5.44	4.83	4.90	4.86	4.84	5.03	.27
2-Methyl Pentane	2.74	1.99	1.89	1.89	1.91	1.91	2.06	.34
2,4-Dimethyl Pentane	1.01	0.36	0.37	0.57	1.19	0.64	.69	.34
2,3-Dimethyl Pentane	2.52	2.66	2.69	2.85	2.97	2.48	2.70	.19
Toluene	8.31	8.15	8.05	7.80	8.49	8.62	8.24	.30
Ethyl Benzene	4.88	4.31	4.30	5.03	5.19	5.08	4.80	.39
m & p Xylene	16.75	15.81	15.90	18.43	19.37	18.12	17.40	1.46
o-Xylene	3.48	3.78	3.55	4.68	4.53	4.05	4.01	0.50
1,3,5-Trimethyl Benzene	0.76	0.43	0.44	0.52	0.47	0.44	0.51	0.13

3.1.5 Calibration for C_2 to C_{10} Hydrocarbon Analysis

Calibration was conducted with both column system used in the C_2-C_{10} hydrocarbon analysis. Standard mixtures of hydrocarbons (minimum purity of 99.0%) in hydrocarbon free air were used to determine response factors incorporated in the analysis methods of the PEP-1 integration system. Table 3 lists those hydrocarbons investigated with their respective response factors.

3.2 BECKMAN 6800 - AIR MONITORING CHROMATOGRAPH

Analyses of carbon monoxide (CO), methane (CH_4), and total hydrocarbons (THC) were conducted on the Beckman 6800 chromatograph according to the work plan in Appendix A. Throughout the task order period, it was used primarily for atmospheric sample analyses and quality assurance checks of standards used by EPA in the RAPS program. The C_2 hydrocarbon analysis was deleted on the 6800 chromatograph due to the lack of sensitivity and peak broadening at low concentrations, resulting in inaccurate results.

3.2.1 Reproducibility Study of Beckman 6800 Chromatograph

To determine the accuracy and precision of the 6800 chromatograph, experiments were conducted to determine linearity, reproducibility and effects on detector response by the sample. Accuracy of the 6800 chromatograph is assured with periodic five point calibrations of THC, CH4, and CO analysis. Figures 4 and 5 contain graphs of the calibrations conducted in July. Linearity checks of the attentuator indicate an error between the attenuation setting, therefore, all samples were analyzed at the same attenuation as the daily standard calibration.

3.2.2 Determination of Precision of Beckman 6800 Chromatograph

Precision of the 6800 analysis was determined by repetitive analysis of an atmospheric bag sample, collected over St. Louis 12 August by the Battelle Research Aircraft. The results of this experiment are tabulated in Table 4 as peak height response of THC, CO and CH_4 found in the sample.

3.2.3 Effect of Sample Characteristics on Flame Ionization Detector

The flame ionization detector response was found to be effected by various sample characteristics. Matrix effects of air vs nitrogen with the THC analysis was substantiated with mixtures of a Scott gas standard (2 pmm CH_4 and 1 ppm C_2 hydrocarbons in air) with hydrocarbon free air and nitrogen. Results of this test are shown in Figure 6 as THC response, with a twenty percent difference in response between them. The matrix effect was also investigated with the CO-CH_4 analysis and was not found to have any effect in the analysis. Response differences/molecular weight for various hydrocarbons was investigated with mixtures of each hydrocarbon (99% minimum purity) in ultrapure air.

TABLE 3

RESPONSE FACTOR DETERMINATIONS FOR PE900 CHROMATOGRAPH

Component	Concentration (ppb)	Standard			Average Response Factors
		1	2	3	
Ethane	200	33.78	34.58	35.14	11.60
N-Propane	200	49.78	50.11	49.51	12.07
N-Butane	200	67.81	72.48	68.00	11.52
N-Pentane	972.1	409.2	430.85	409.8	11.67
N-Hexane	857.3	443.01	410.65	415.39	12.16
2.4-DM Pentane	751.9	420.33	432.10	421.38	12.40
Toluene	1053.9	539.00	589.82	527.72	13.36
m-Xylene	916.2	514.43	528.91	579.49	13.55
1,3,5-TM Benzene	805.2	527.77	464.29	580.09	13.83
n-Butyl Benzene	717.8	586.76	557.35	521.36	12.93

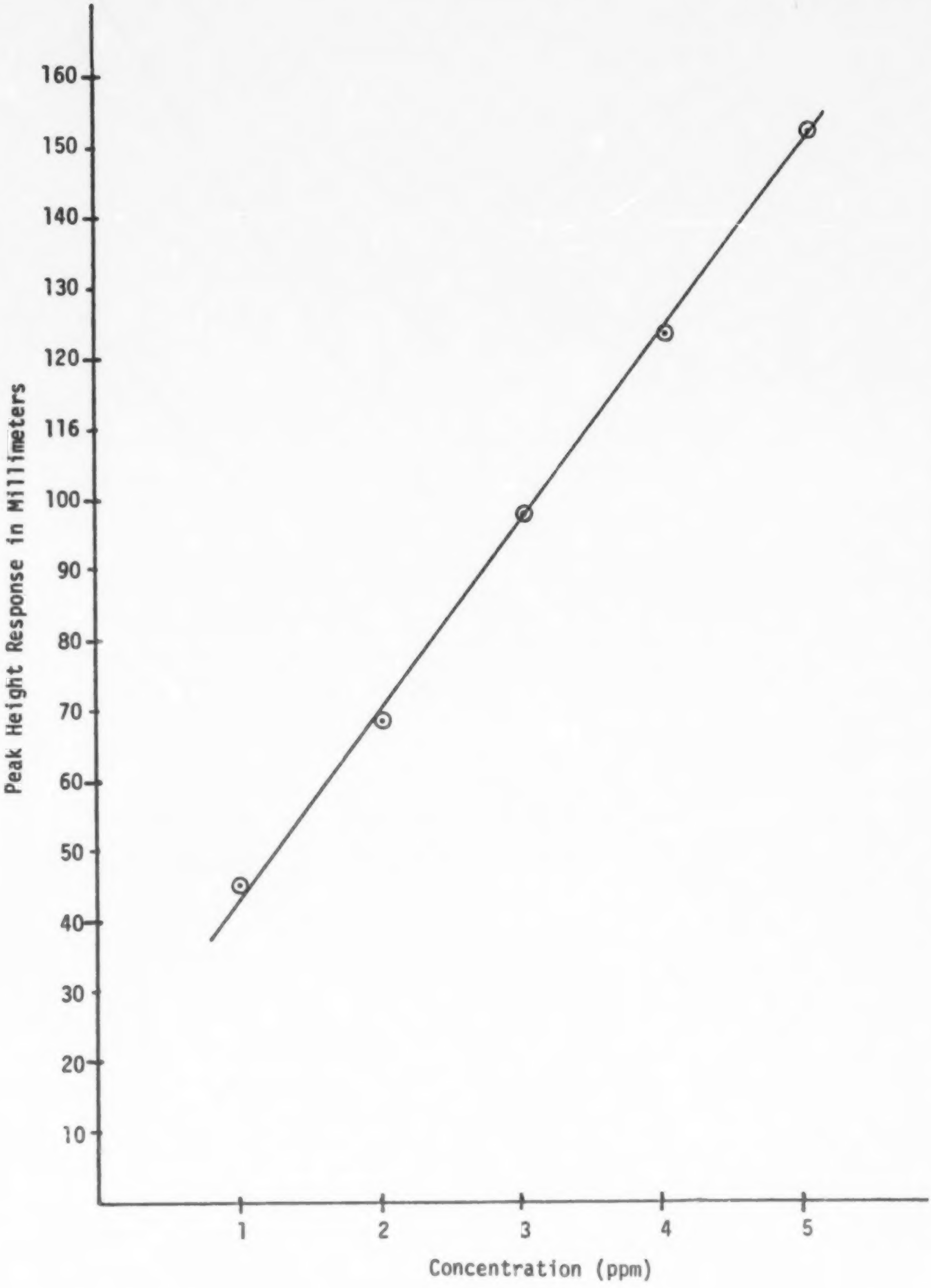


FIGURE 4

FIVE POINT CALIBRATION OF TOTAL HYDROCARBON ANALYSIS

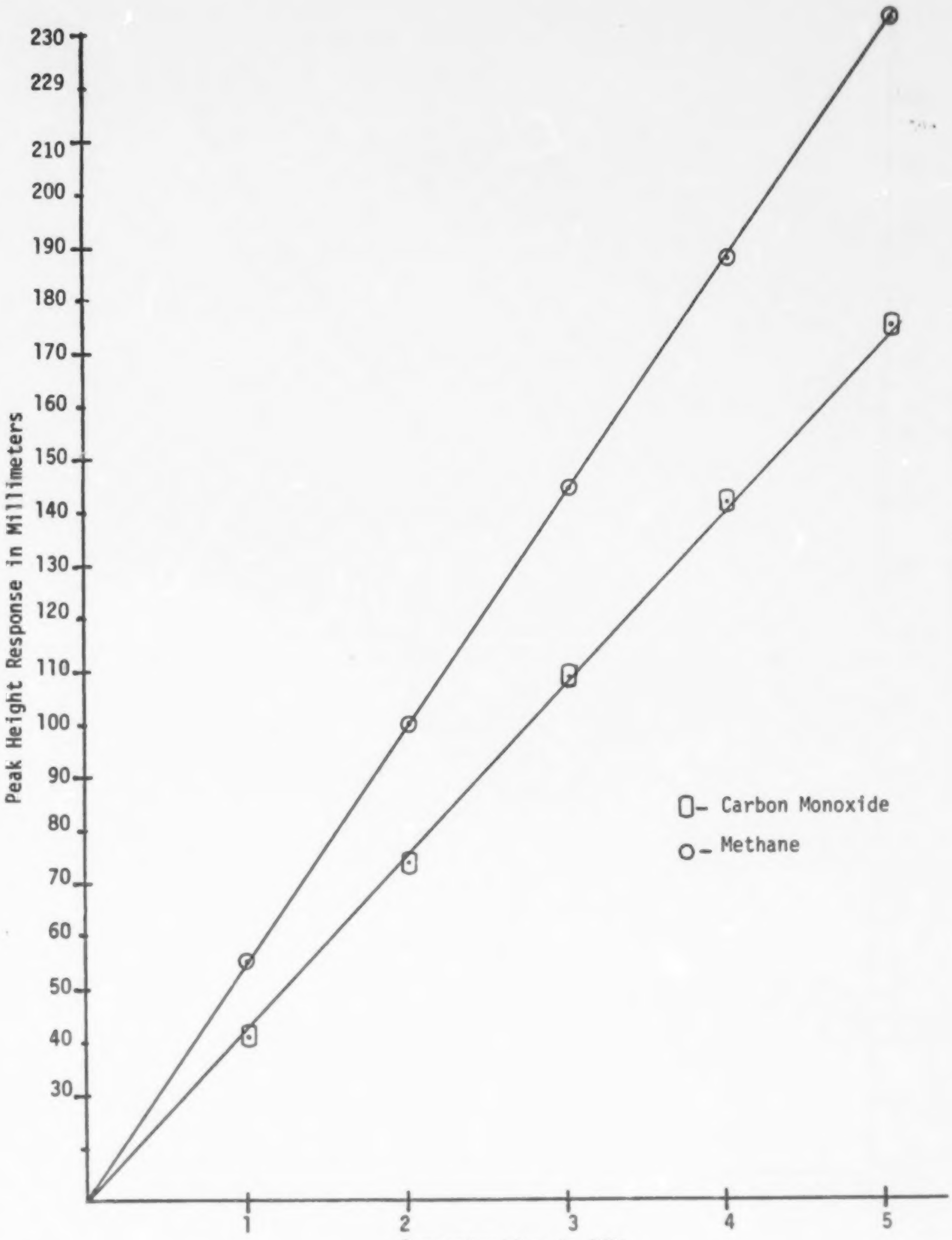
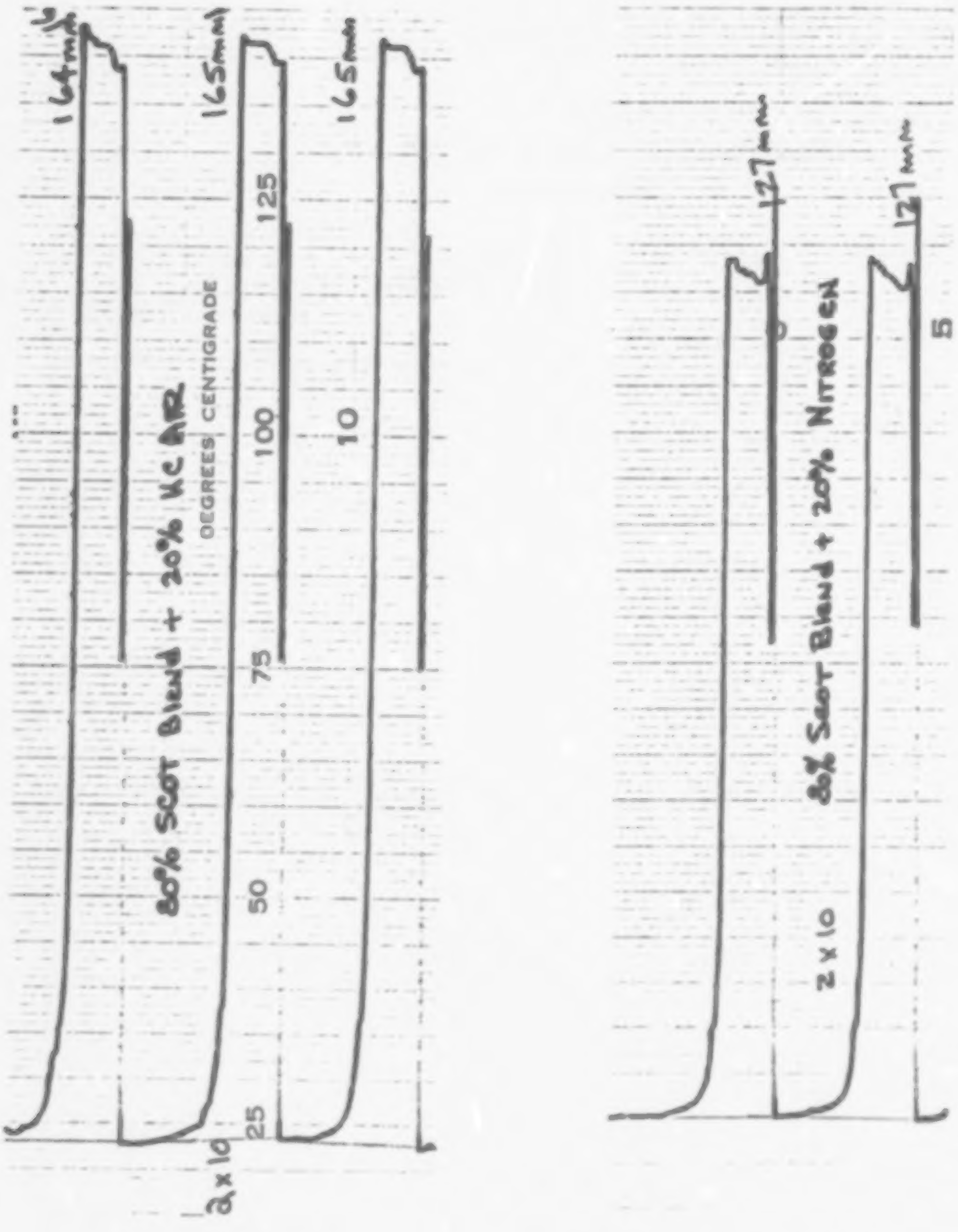


FIGURE 5
FIVE POINT CALIBRATION OF CO AND CH_4 ANALYSIS

TABLE 4

REPRODUCIBILITY STUDY OF BECKMAN 6800 CHROMATOGRAPH

RVN	Total Hydrocarbon Analysis (mm-Peak Height)	Methane (mm-Peak Height)	Carbon Monoxide (mm-Peak Height)
1	116.1	62.7	22.3
2	116.9	62.3	21.9
3	116.3	62.9	21.4
4	115.7	62.2	21.3
5	116.3	62.1	21.1
6	115.3	62.1	22.0
7	115.3	62.2	21.3
8	115.7	62.6	21.3
9	116.3	62.0	21.1
10	115.9	62.0	21.2
$\bar{X}$	115.98	62.31	21.49
S_x	0.50	0.31	0.42



80% Scot Blend
+
20% Hydrocarbon Free Air

80% Scot Blend
+
20% Nitrogen

FIGURE 6
EFFECTS OF SAMPLE MATRIX ON
TOTAL HYDROCARBON ANALYSIS

Table 5 contains the results of this experiment, indicating variations in THC response of 7 to 51 percent lower than methane. Adjustment of the flame detectors air and hydrogen mixture to minimize the differences proved only to cause flame outs in sample injection.

3.2.4 Effects of Total Hydrocarbon Analysis by Tedlar Bag

Parallel to sample effects on flame response is the desorption problems with Tedlar bags used in helicopter sampling. Distorted THC response and secondary peaks were found in THC analysis of atmospheric samples collected in Tedlar bags. During the February intensive period, THC measurements were deleted from all helicopter samplings using Tedlar bags.

3.2.5 Effects on CO-CH_4 Analysis By Contaminated Hydrogen Carrier Gas

The CH4-CO analysis was also affected by problems of methane contamination in the hydrogen carrier gas of the 6800 chromatograph. Negative responses in the CH4-CO analysis occur when the purity of the sample is greater than the hydrogen carrier. Control of this problem is achieved by changing the molecular sieve 5A drier, but is short term as the methane will diffuse through with time. A hydrogen generator is recommended to prevent this problem and as an alternative to costly high purity hydrogen gas.

3.3 BENDIX TOTAL OXIDES OF NITROGEN (NO_x) ANALYZER

The Bendix NO_x Analyzer was operational 6 February and used continuously throughout the remaining Task Order period for total oxides of nitrogen measurement. Nitric oxide (NO) was not analyzed in atmospheric bag samples due to the thermal degradation of NO during transfer of the sample to the laboratory.

3.3.1 Improvements in Response and Accuracy

A few adjustments were made to improve the response of the NO_x analyzer. The response time was improved with the interchange of the inlet line with the exhaust line to the reaction chamber. Oxygen ($<$ 10 ppm moisture) was used for Ozone generation because of the zero offset that occurs when insufficient moisture is present.

3.4 TRACOR 270 - SULFUR CHROMATOGRAPH

The sulfur chromatograph was not used throughout the Task Order period due to the adsorption of sulfur compounds with Teflon and Tedlar material. Graph of depletion of SO_2 in a Tedlar bag due to absorption is contained in Figure 7. The sulfur chromatograph was maintained operational by the performance of periodic calibration and maintenance.

TABLE 5
TOTAL HYDROCARBON RESPONSE DIFFERENCES/MOLECULAR WEIGHT

Component	Concentration (ppm)	THC Response (mmPeak Height)	Normalized Response (1)	Percent Difference From Methane
Methane	4.66	130	130	
Ethane	4.0	154	90	31
Ethylene	4.00	117	68	48
Acetylene	4.00	236	138	6
Propane	4.00	232	90	31
Propylene	4.00	170	66	49
Isobutane	3.00	230	89	32
2-Methyl Pentane	1.64	138	59	55
Toluene	2.00	272	90	31
m-Xylene	1.83	238	76	42

(1) Response normalized to methane in concentration and carbon number.

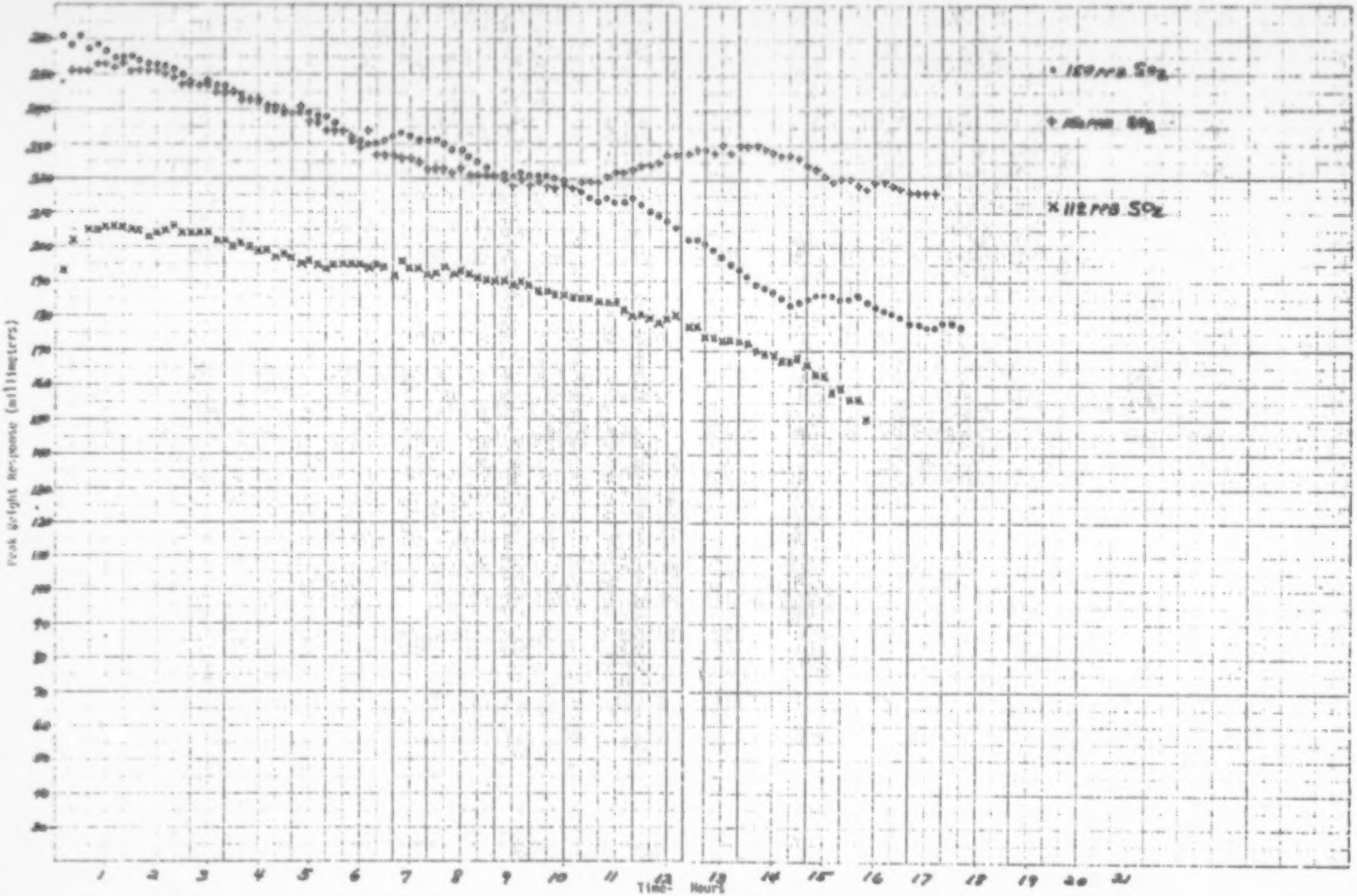


FIGURE 7 - DEPLETION RATE/TIME OF SO_2 IN TEDLAR BAG

3.5 VARIAN 460 CHROMATOGRAPH - ELECTRON CAPTURE DETECTOR

The Varian 460 chromatograph with an electron capture detector is intended for the analysis of fluorocarbons (Fluorocarbons 11 and 12 and SF_6) to the part per trillion level. Methods for the analysis of the fluorocarbons mentioned were established during the latter part of the Task Order but detection limits of 500 ppt for fluorocarbons and 20 ppt for SF_6 was achieved. Figure 8 is a diagram of the sampling and column system used in the two analyses. Note that the SF_6 analysis is conducted on the molecular sieve 5A analysis column with a stripper used to remove heavy hydrocarbons and water. The fluorocarbons 11 and 12 are separated with the silica gel column. Typical chromatograms of the two analyses are shown in Figures 9 and 10.

3.6 BENDIX DYNAMIC CALIBRATION SYSTEM AND PURE AIR SYSTEM

Both systems were operative from February and used throughout the Task Order period in calibration of the Bendix NO_X analyzer and Tracor sulfur chromatograph. Calibration is conducted with NBS certified SO_2 permeation tubes and an Airco 100 ppm NO gas standard, standardized with an NBS certified NO gas standard. Periodic checks of the dynamic calibration system are conducted for linearity and flow rates of the capillary dilution system. Figures 11 and 12 illustrate the linearity check conducted in July, with graphic description of flow rates (cc/min) vs inlet pressure (1 lb.) to the capillaries.

3.7 EVALUATION OF SAMPLE BAG MATERIALS

Atmospheric samples are collected in Teflon and Tedlar bags for analysis of various pollutants. Evaluation of the bag materials was conducted to establish the hydrocarbon desorption in storage. The bags were purged with helium gas (99.9999% purity) and filled with zero grade air (of known purity). The bags were analyzed for total hydrocarbons (THC) on the 6800 chromatograph, capped and stored. Re-evaluation of the THC is conducted after a predetermined time.

3.7.1 Tedlar Material Evaluation

Tedlar material was proposed for use in atmospheric sampling because of ease in sealing and repair of the bag seams. Evaluation of Tedlar indicated a high THC build-up with distorted THC response and secondary peaks. Attempts were made to minimize the THC increase by heating the Tedlar in an oven at 100° and evacuating, and to wash the inside walls of the bag with an ionic detergent. Neither test was able to correct the problem, and the Tedlar bags were limited to only CO and CH_4 analysis of helicopter sampling. Results of the investigations of Tedlar for bag desorption time are contained in Table 6.

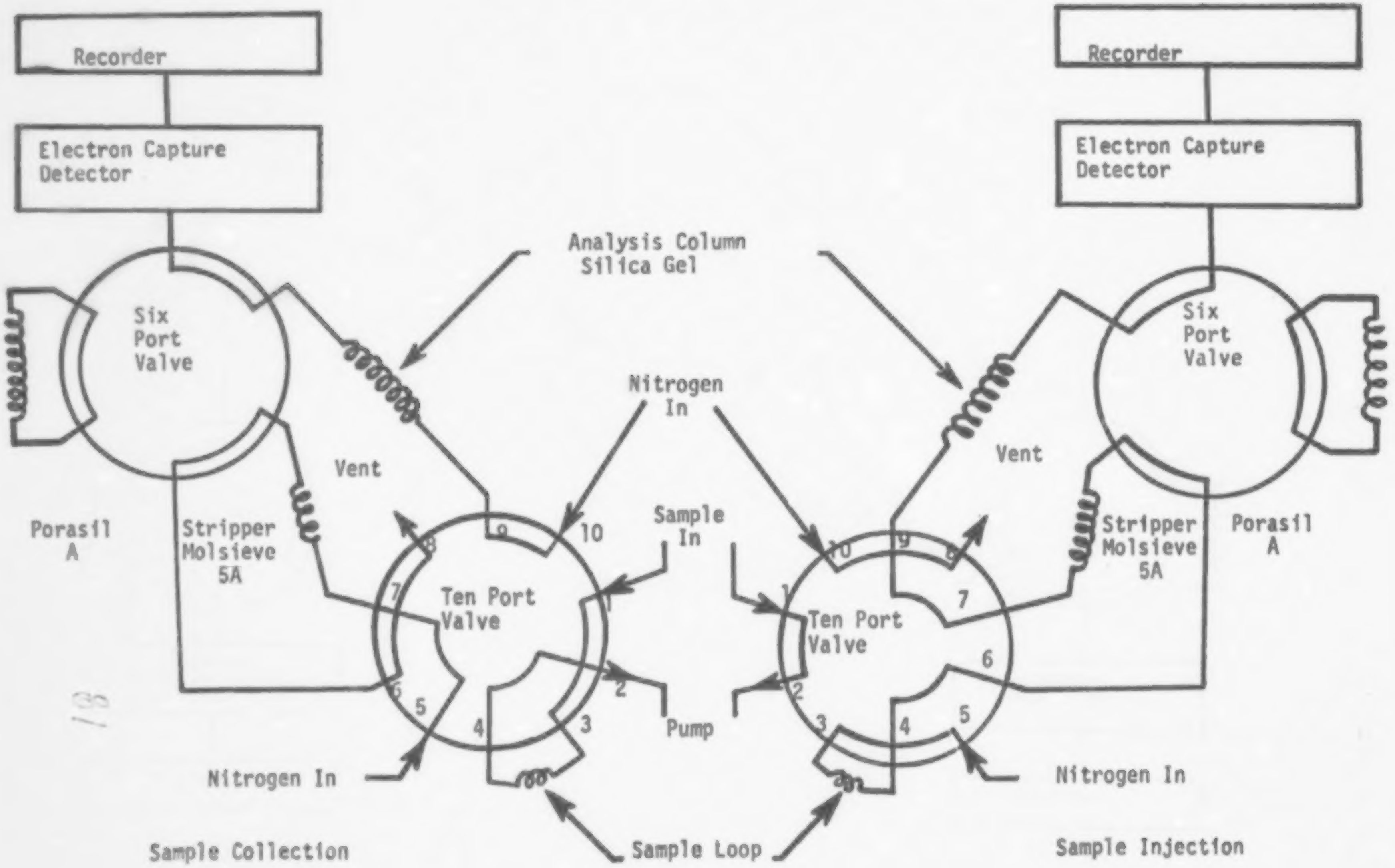

Recorder
Electron Capture Detector
Six Port Valve
Porasil A
Stripper Molsieve 5A
Vent
Ten Port Valve
1
2
3
4
5
6
7
8
9
10
Nitrogen In
Sample Collection
Analysis Column Silica Gel
Nitrogen In
Sample In
Pump
Sample Loop
Recorder
Electron Capture Detector
Six Port Valve
Vent
Stripper Molsieve 5A
Porasil A
Ten Port Valve
1
2
3
4
5
6
7
8
9
10
Nitrogen In
Sample Injection

FIGURE 8 - SF_6 ANALYSIS CONFIGURATION

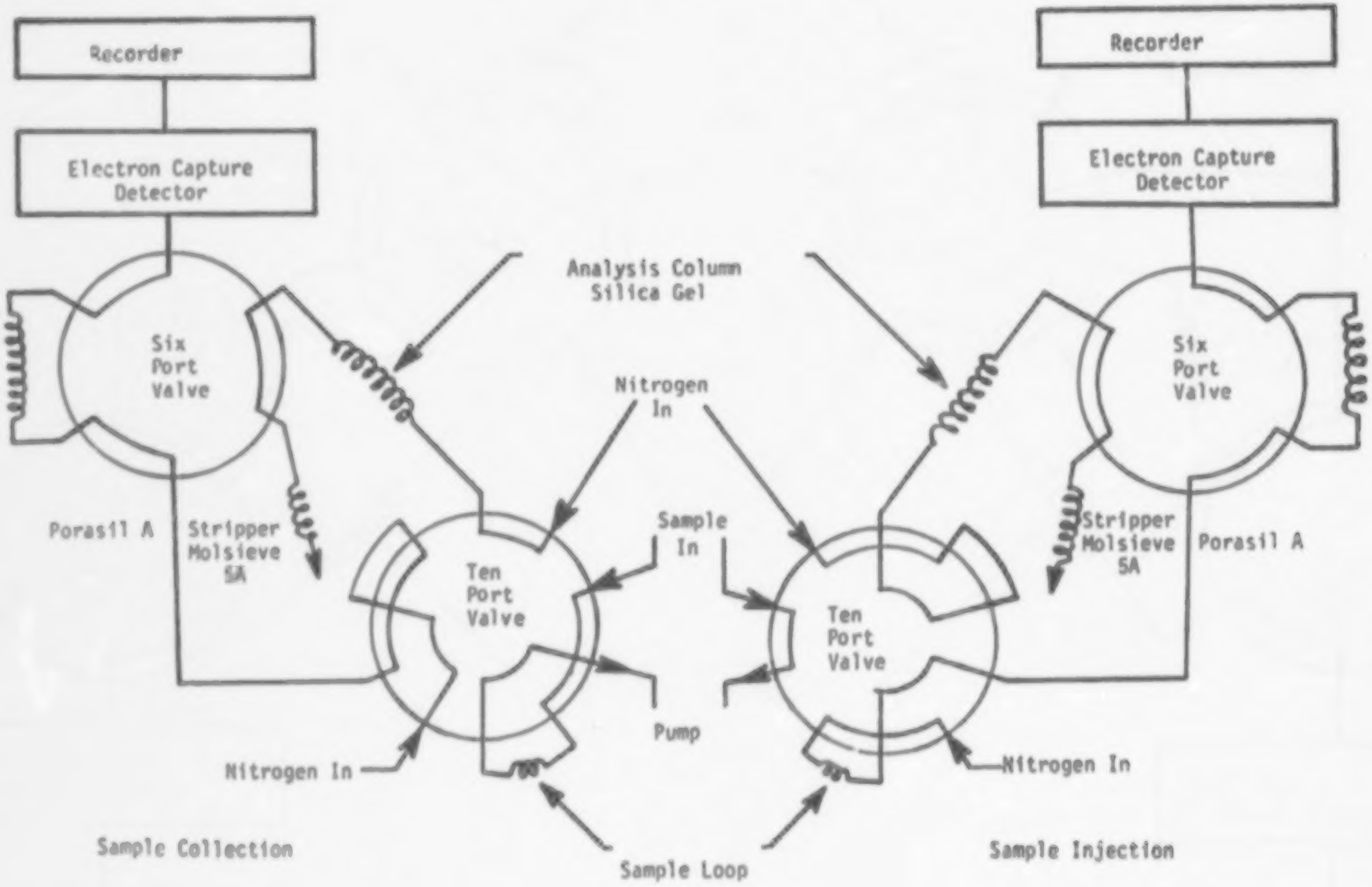
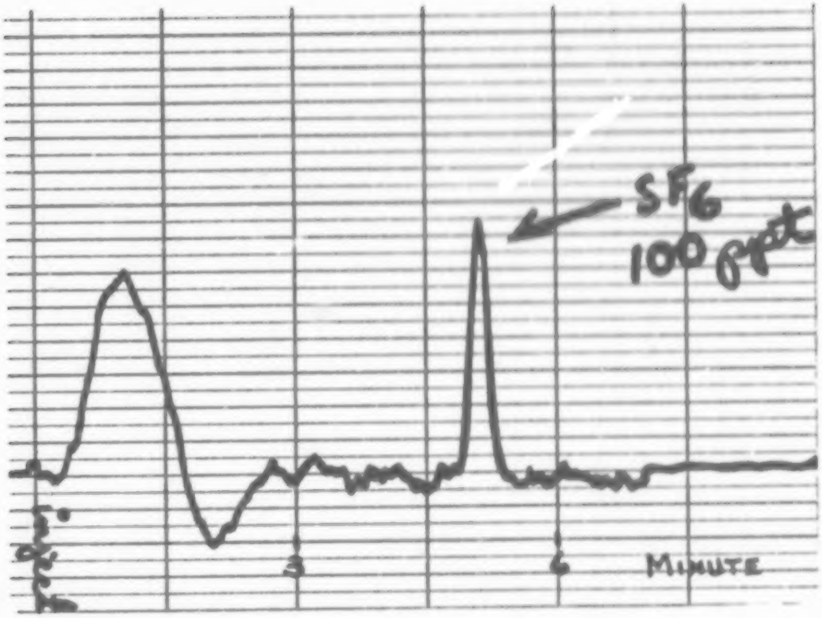

Recorder
Electron Capture Detector
Six Port Valve
Porasil A
Stripper Molsieve 5A
Ten Port Valve
Nitrogen In
Sample Collection
Analysis Column Silica Gel
Nitrogen In
Sample In
Pump
Sample Loop
Recorder
Electron Capture Detector
Six Port Valve
Stripper Molsieve 5A
Porasil A
Ten Port Valve
Nitrogen In
Sample Injection

FIGURE 8A - FLUORO-HYDROCARBON ANALYSIS CONFIGURATION

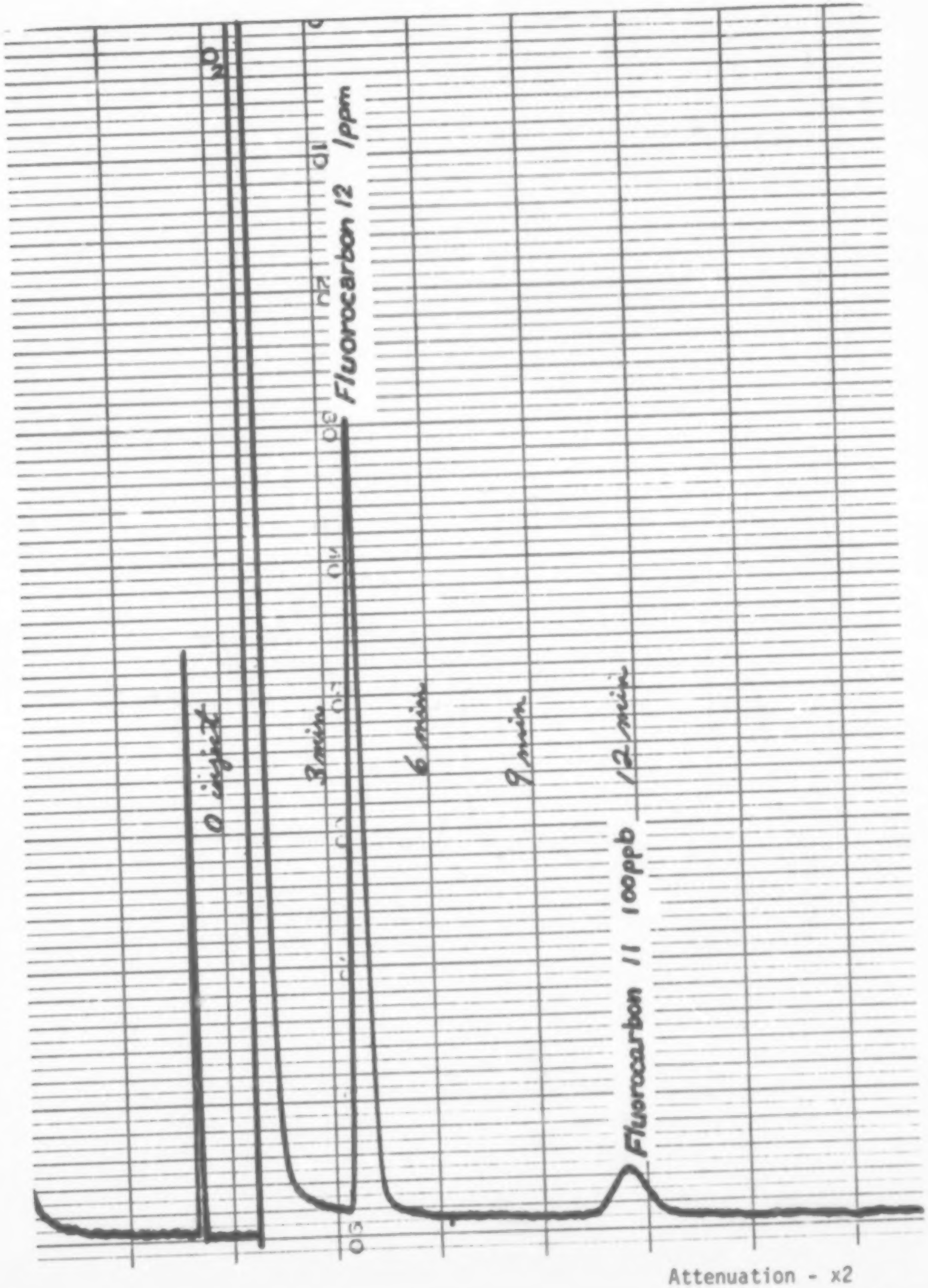


Attenuation - x4

Range 10^{-10} amps/$_{mv}$

FIGURE 9

CHROMATOGRAM OF SF$_6$ ANALYSIS



Attenuation - x2

Range - 10^{-10} amps/m

FIGURE 10 - CHROMATOGRAM OF FLUOROCARBONS 11 AND 12 ANALYSIS

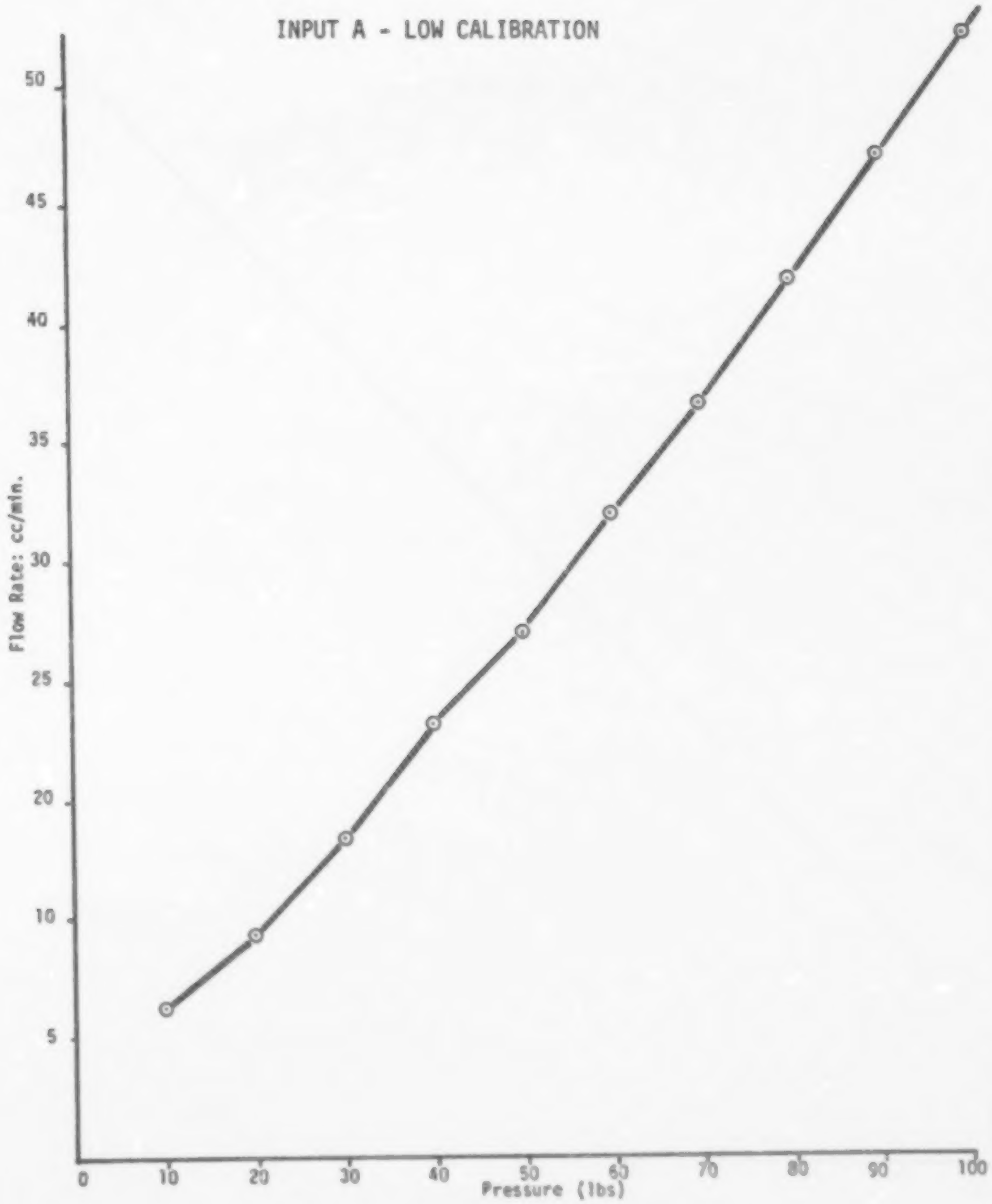


FIGURE 11 - CALIBRATION OF BENDIX

DYNAMIC CALIBRATOR CAPILLARY SYSTEM

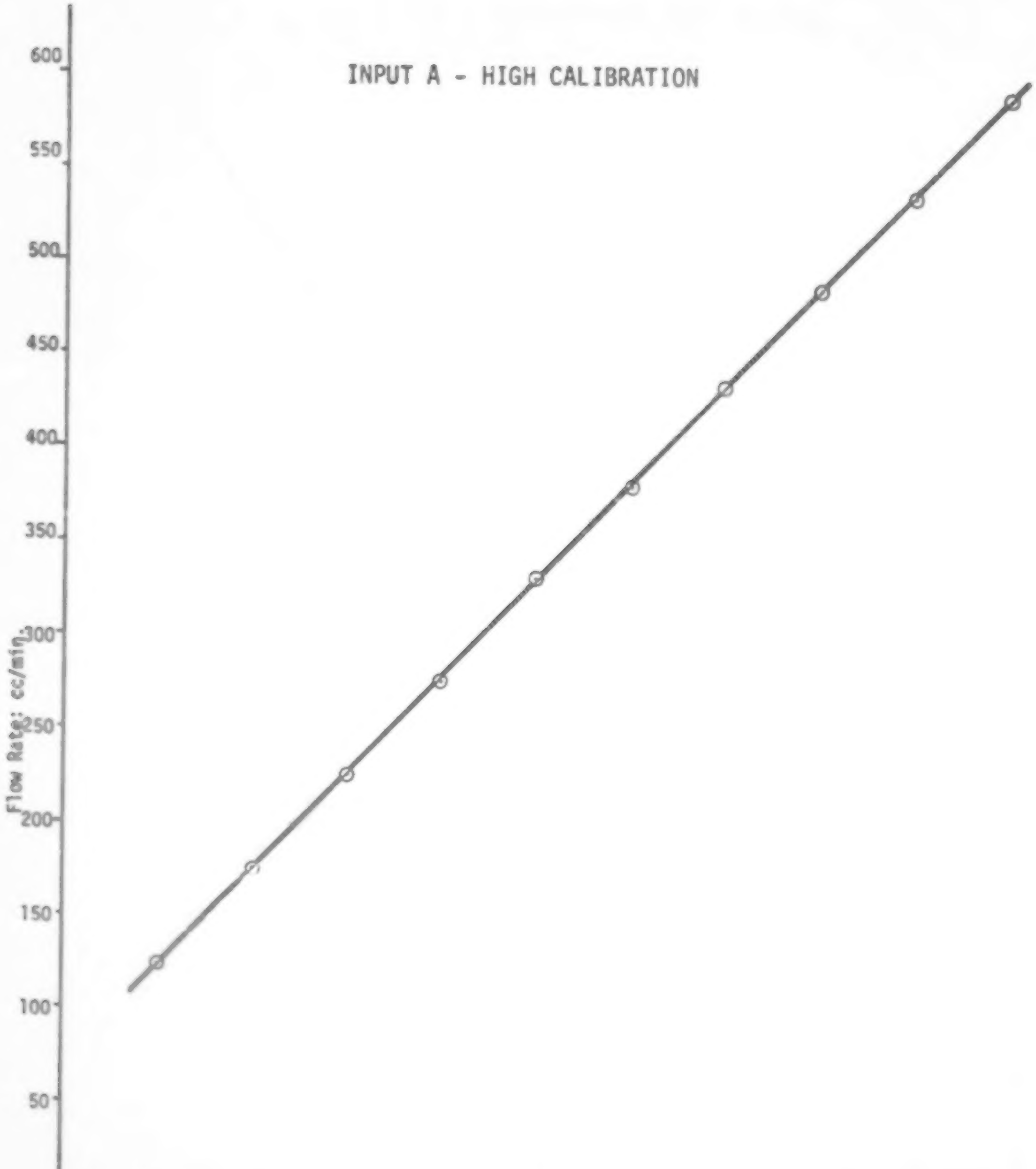


FIGURE 12 - CALIBRATION OF BENDIX

DYNAMIC CALIBRATOR

TABLE 6 RESULTS OF TEDLAR BAG DESORPTION/TIME

Material Tested	Total Hydrocarbon (ppm) Increase/Time				Increase In Total Hydrocarbons (ppm/Hr)	Remarks
	Initial	24 Hrs	48 Hrs	72 Hrs		
Used Tedlar Helicopter Bag May 5-7	0.096	0.143	0.226		0.003	Helium Purged-Filled Linde Hydrocarbon Free Air
New Tedlar						No Helium Purge-Filled with Linde Hydrocarbon Free Air
Bag 1	0.053			0.212	0.002	
Bag 2	0.059			0.247	0.003	
Bag 3	0.057			0.125	0.001	
May 7-11						

3.7.2 Teflon Material Evaluation

Teflon is presently used as the bag material in sampling at the RAMS sites. Two mil thickness is used but forms seam leaks with extensive sampling and handling. As an alternative, five mil Teflon bags were investigated for material desorption/time and leakage. The tests were conducted in a similar manner to the Tedlar evaluation, and the results are tabulated in Table 7, comparing 2 mil Teflon to various 5 mil material and manufacturers.

3.7.3 Bag Leak Test Modification

In the evaluation of the bag materials, a second criteria was determined, leak rate/time. Initially the leak test procedure was per the one outlined in the Work Plan (Appendix A). Variations to this procedure were incorporated because with applied weight and 100 liter volumes the possibility of seam flexing and leakage occurred. The new procedure entails a 60 liter quantitative fill with no applied weight and a 10% leakage allowable on quantitative evacuation. The number of 2 mil Teflon FEP-L bags received and found acceptable were 232 and 122, respectively.

3.8 QUALITY CONTROL

Quality control procedures followed in the Gas Chromatography Laboratory are outlined in the Work Plan. Quality control standards used daily in the laboratory are certified periodically with NBS standards when available, e.g., NOX and CO. Where NBS certification is not available, laboratory standards are prepared of quantitative mixtures of pure hydrocarbons with ultra pure air. Replicate standards are made up and their average response factors taken to determine concentrations of the other quality control standards.

3.8.1 Carbon Monoxide Depletion/Time in Quality Control Standards

Monthly checks of the CO concentration of the Quality Control standard indicated a gradual decrease in the CO concentration. Because the CO standard is made up in a steel cylinder, iron carbonyl ($Fe_2(CO)_9$) is suspected to form and CO depleted. Figure 12 graphically shows the loss of CO with time. Presently, CO standards in aluminum cylinders are used in the laboratory, and their concentration monitored periodically.

TABLE 7 RESULTS OF TEFLON BAG EVALUATION

aterial nd acturer	Date of Test	Total Hydrocarbon (ppm) Increase/Time							Increase In THC (ppm/Hr)	Remarks
		Initial	24 Hrs	48 Hr	72 Hr	96 Hr	144 Hr	240 Hr		
on Type il Xonics	6/3 To 6/6	0.16			1.22				.015	Helium Purged-Filled With Scott Marion Ultra Pure Air
on Type L	5/16 To 5/20	0.02				2.10			.022	Initially Filled With Pure Air
can ilm Co.	5/23 To 5/26	1.06			1.42		170 Hr		.004	Bag was heated @ 100° C For 1 Hour Prior To Refilled With Ultrapure Air
Type L ton Co.	5/28 To 6/2									Purged With Helium and Filled With Scott Marion Ultrapure Air
		0.16		5.99				10.92	0.045	
		0.16		7.46						Bag 2 Sample Deplete On Analysis At 240 Hours
		0.16		5.79				10.30	0.042	

TABLE 7 (CONTINUED)

Bag Material And Manufacturer	Date of Test	Total Hydrocarbon (ppm) Increase/Time							Increase In THC (ppm/Hr)	Remarks
		Initial	24 Hrs	48 Hr	72 Hr	96 Hr	144 Hr	240 Hr		
Tefzel Type A 5 Mil (Small Bags)	5/28 To 6/2									Purged With Helium And Filled With Scott Marion Ultrapure Air
Livingston Co.										
Bag 1		0.16		5.18				9.84	0.040	
Bag 2		0.16		6.29						Bag 2 Sample Depleted On Analysis @ 240 Hours
Bag 3		0.16		4.97				9.17	0.038	
Tefzel Type A 5 Mil	6/11 To	0.21	2.55	3.45					0.068	Both Bags Had Squared Seams Helium Purged & Filled With Scott Ultra Pure Air
Teflon Type L 5 Mil		0.21	0.78	1.19					0.020	
Tefzel Type A 5 Mil	6/11 To 6/13								0.032	Both Bags Had Flat Seams Helium Purged And Filled With Scott Marion Ultra Pure Air
Bag 1		0.21	1.19	1.74						
Bag 2		0.21	0.99	1.40					0.025	
Teflon Type A 5 Mil American Durafilm Co	8/8 To 8/12	0.10				1.71			0.017	Helium Purged Filled With Linde Hydrocarbon Free Air

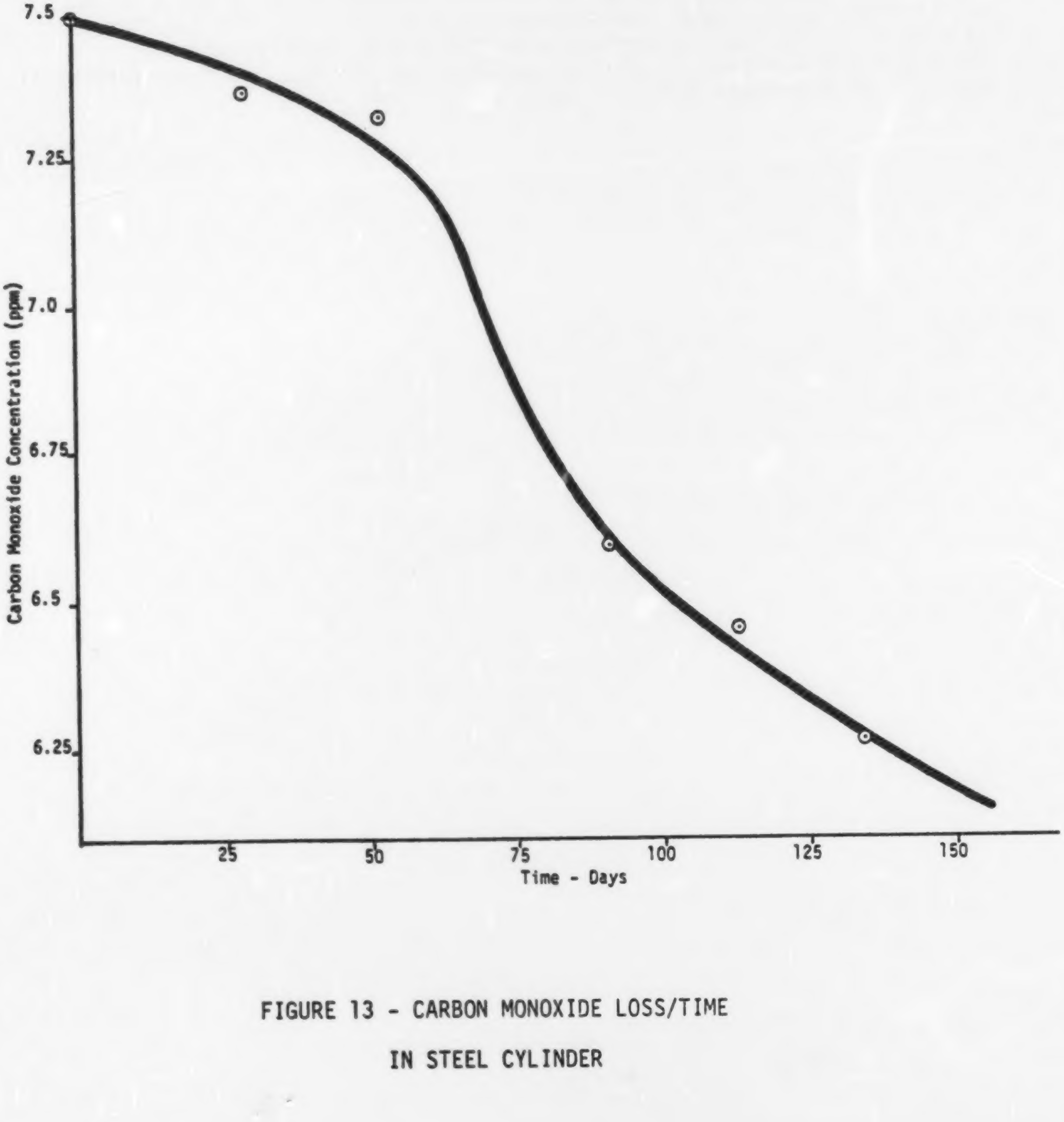


FIGURE 13 - CARBON MONOXIDE LOSS/TIME

IN STEEL CYLINDER

4.0 SUMMARY

The Gas Chromatography Laboratory is completely operational, with quantitative analysis established for C_1 to C_{10} hydrocarbons, total oxides of nitrogen, carbon monoxide, and total hydrocarbons. Sensitivity of 0.1 parts per billion for C_1 to C_{10} hydrocarbons has been achieved with carbon monoxide and total oxides of nitrogen determined to 10 and 5 parts per billion, respectively. Halogenated organic compounds, SF_6 and fluorocarbons 11 and 12, were determined with an electron capture detector. Sensitivity of 0.1 part per billion was obtained for SF_6, but fluorocarbons 11 and 12 were detectable above 500 parts per billion.

APPENDIX I

GAS CHROMATOGRAPHY LABORATORY WORK PLAN

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RAPS GAS CHROMATOGRAPHY LABORATORY

WORK PLAN

1.0 INTRODUCTION

The St. Louis Regional Air Pollution Study is being conducted to develop, evaluate and validate air-quality simulation models for both regional and local scales covering urban and rural areas of stationary and mobile pollution sources. In addition, a comprehensive, accurate and readily retrievable data base of pollutants is being developed for RAPS and future simulation and effects of model testing and validation. The RAPS Gas Chromatography Laboratory is established to support a variety of studies under the program; e.g., A. Evaluation of the Regional Air Monitoring Station (RAMS) sites; B. Validation of Automotive Emissions inventory submodels; C. Defining the Composition of Emissions from significant sources; D. Tracking Plumes; and E. Developing and Validating Photochemical Sub-models.

The Gas Chromatography Laboratory collects and performs analysis of atmospheric samples for a variety of pollutants, including hydrocarbons, carbon monoxide, and atmospheric tracer gases. Supplemental analyses for sulfur compounds and nitrogen-oxides are also conducted. The data produced from analysis is validated for quality-assurance, recorded on magnetic tape and inputed to the RAMS/RAPS Computer Data Bank, Research Triangle Park, North Carolina.

2.0 LABORATORY CAPABILITIES AND ANALYSIS PROCEDURES

The Gas Chromatography Laboratory is equipped and staffed to perform specific analyses of air samples as follows:

1. Hydrocarbon Analysis

The C_2-C_{10} hydrocarbon analyses are conducted on a Perkin-Elmer, model 900 gas chromatograph, using a glass bead concentration system with separation of the hydrocarbons with a two column system. C_1 to C_4 hydrocarbons are determined with a packed column, while the C_4 to C_{10} hydrocarbons analysis is achieved with a 200 foot capillary column. The procedure for operation, sample introduction and analysis follows:

A. Preparation of Chromatograph

1. Establish column flow rates of helium carrier gas using a bubble flow meter:
   a. Capillary column @ 12 ml/min.
   b. Packed column @ 40 ml/min.
2. Turn on H_2 and air source, 16 lb. H_2 @ inlet gauge and 50 lb. on air regulator. Light flame ionization detectors noting base line shift on recorder when lite.

3. Packed column is held at room temperature, while capillary is set at 20° and held for six minutes, then 16°/min. temperature program rate, for 5 minutes to 100°C. Initiate pressure programming after 100°C has been achieved.

4. Initiate cooling of the capillary column by turning on liquid nitrogen at dewar.

5. Fill concentration traps with liquid oxygen.

6. Enter directives of identification, time of analysis, and threshold values on teletype to the PEP-1 integrator.

7. Zero recorders with both electrometers, set on range 1, x1 for analysis.

B. Introduction of Sample into Concentration Traps

1. Assure the identity of the bag to be analyzed has been logged in the PE 900 Operational Logbook as to the time, date, location, and type (helicopter, site, etc.).

2. Connect quick disconnect fitting to the inlet of the sample bag.

3. Connect appropriate vacuum line to the constant volume cylinder attached to the vacuum pump (refer to Figure 1).

4. Connect bag sample to appropriate inlet line and open vacuum source to draw a half liter of sample through the inlet lines (allowing purging of the line of air from the previous sample).

5. Close the inlet valve to the constant volume cylinder and evacuate to 10 mm Hg. with the vacuum pump.

6. Close the vacuum pump valve and open the inlet valve to draw the air sample from the air bag sample through the sampling system.

7. Switch the inlet valve to trapping mode and note starting position on vacuum gauge at the constant volume cylinder. Introduce an accurately measured volume of sample (400 to 500 cc.) through the concentration trap, and switch the valve back to the backflush position.

8. Disconnect the bag and store.

C. Injection and Analysis of Bag Sample

1. After the sample is trapped, switch the second valve to injection mode and heat the trap with hot water (90°C).

2. Immediately, actuate ready light on PEP-1 interface, start light to initiate temperature programming (capillary column analysis only), and a start position on the recorders.

3. The second valve is returned to the backflush position once ethylene has eluted from the column.

4. Continue the analysis for fifteen minutes with the packed column analysis and for 60 minutes with the capillary analysis.

5. Maintain the capillary column at 100° while pressure programing to 60 lb. inlet pressure.

6. After elution of the C_{10} hydrocarbons, switch the backflush valve until heavy hydrocarbons greater than C_{10} molecular weight have eluted from the column (note peaks on chromatogram).

7. Press the compute buttons on the interface modules to tabulate the area measurement concentration and identification of the peaks found in the chromatogram.

8. Press the reset button on the front of the chromatograph to cool the capillary column and refill the concentration traps with liquid oxygen for resampling.

9. A single analysis of each bag sample will be performed with a duplicate analysis at the end of the day of the first sample analyzed from each set of samples to insure reproducibility of the trapping system. The concentration of the hydrocarbon components in the sample are determined to the nearest 0.2 ppb carbon by direct comparison of area response with the standard response factor for that component.

D. Calibrations

Daily calibrations and periodic calibrations are performed to assure instrument performance and data accuracy. All calibration data is logged in the operational Log Book and incorporated in the daily analysis of air bag samples.

1. Daily Calibration

A quantitative calibration is performed daily before analysis of test samples by:

a. Introducing into the chromatograph the quality control standard gas mixture of fourteen hydrocarbons (C_2 - C_{10}) in air. Calibration is performed with both column systems.

b. Comparison and verification of retention times for each component of the quality control standard will be conducted and average response factors determined for each class of hydrocarbon compound.

2. Periodic Calibration

a. Pressure gauges and rotameters on the chromatograph will be functional checked every six months.

b. A linearity check of the 1mv dual pen recorder will also be conducted every six months.

E. Maintenance conducted will be logged in the Maintenance Log Book under Section for the PE 900.

1. Once a month the charcoal scrubber on the helium carrier cylinder is regenerated @ 200° for 24 hours.

2. Leak check of the chromatograph and pressure programmer will be conducted every three months.

3. System is serviced when duplicate analysis or response factors exceed ten percent variation.

F. Hardware

1. The Perkin-Elmer PE900 Chromatograph is equipped with dual flame ionization detectors, dual electrometers, and temperature programmer.

2. Utilized with the PE900 is the Perkin-Elmer PEP-1 computer integrator with dual channels for interfacing with the dual detector system.

3. The pressure programmer is an Analog Flogramer.

4. The analysis columns consist of a 200 ft. x 1/16 inch support coated open tubular squalane capillary, and a packed column of 80/100 mesh acid washed silica gel, 5 ft. x 1/8 inch.

5. The inlet valve system indicated in Figure 1 (see page 9) is a stainless steel body with Teflon diaphrams.

6. Gases used with the PE900 are:

a) Helium supplied by the Bureau of Mines and purified with a charcoal drier.

b) Air, zero-grade of maximum 2ppm hydrocarbon and 3ppm moisture.

c) Hydrogen, zero-grade of 99.99% purity with maximum hydrocarbon of 1ppm.

7. All connecting lines and fittings are either Teflon or stainless steel.

2. Carbon Monoxide, Methane and Total Hydrocarbon Analysis

Analysis of carbon monoxide, (CO), methane, (CH_4), and total hydrocarbons are conducted utilizing a Beckman Model 6800 process gas chromatograph. Sampling of all bag samples is accomplished through a pumping system which pulls the sample through the chromatographic system, insuring no dilution or contamination of the sample by the pump system. The procedure for operation and sample introduction and analysis follows:

6800

A. Preparation of Chromatograph

1. Turn on the air cylinder (40# outlet pressure) and check the hydrogen generator for proper water level and 40# outlet pressure.

2. Light flame ionization detector noting the flame out light off and start light on, located on front control panel.

3. Turn on the recorder, set on 10 mv range, and zero with 0 volt button depressed. Actuate auto zero toggle switch on front control to zero electrometer of chromatograph.

4. Set H_2 carrier pressure to give a 25 cc/min flow rate with the C-3 column.

5. Adjust the air carrier to 31-34 cc/min through the total hydrocarbon capillary.

6. Set the detector air and hydrogen fuel to give the maximum total hydrocarbon response.

7. Attach air bag sample on inlet line at the rear of the chromatograph and turn on the pumping system.

B. Analysis of Air Bag Sample

1. Enter all pertinent data of the air bag sample in the 6800 Log Book.

2. After five minutes of drawing the sample through the chromatograph, actuate valve B for twenty seconds to measure the total hydrocarbons in the sample.

3. The attenuation setting is normally set at x2 on range of 10.

4. The methane and carbon monoxide are determined by actuating valve A for forty-five seconds.

5. The attenuation setting will be from x2 to x8 on range of 1.

6. The C_2's can be determined by actuating valve C until completion of the analysis.

7. It is proposed that a C_2 analysis of one of the air bag samples per group of samples collected that day will be analyzed and compared to the results obtained on the Perkin-Elmer 900 Chromatograph.

8. Air samples are analyzed once and the concentration to the nearest 10 ppb carbon determined by comparison of the peak height response of the sample to the standard for that day. First sample of the day is run in duplicate at the end of the day to insure reproducibility.

C. Calibrations

Calibrations performed are tabulated in the Operational Log Book and incorporated daily in bag sample analysis.

1. Daily calibrations

   a. A three-point calibration will be conducted daily using zero air, a 5 and 15 ppm CO standard, and a 5 and 8 ppm CH_4 standard. The 5 ppm standard of CO and CH_4 will be a mixture in air and will allow a check of the separation and condition of the C-3 analyses columns.

   b. Both standard mixtures will be analyzed on the day of sampling and response factors determined from an average response of three analyses.

   c. Once a month, a check of the standard cylinder mixtures will be conducted with gas standards of CO and CH_4 made up in an air matrix of measured CO-CH_4 impurity. This will insure the concentration of the standard and determination of loss due to adsorption on the walls of the cylinder.

   d. The standard mixture used in the 900 calibration will be used for calibration for the C_2's on the day the C_2 comparison analysis is conducted.

2. Periodic calibrations - Every six months will include:

a. Linearity check of the 10 mv recorder

b Functional check of the pressure gauges

c. Five-point calibration

D. Maintenance

Maintenance conducted will be logged in the Maintenance Log Book under the section for the 6800 Chromatograph.

1. Leak check once a month of the inlet gas lines, sampling system, chromatograph valves and plumbing and establish proper flowrates through the system.

2. Check the amplifier board once a month for auto zero and range change linearity.

3. Change the sample inlet filter monthly.

4. Replace the deionizer resin in the hydrogen generator water supply every two months.

5. Replace the moisture absorption columns in the hydrogen generator and on the zero air cylinder.

E. Hardware

1. The Model 6800 Chromatograph is designed for monitoring of six air pollutants, total hydrocarbons, methane, carbon monoxide, ethane, ethylene and acetylene. It is composed of a flame ionization detector, pressure actuated valve introduction system, and a three-column analysis system.

2. The three packed columns are a prestripper column of triton 350 combined with silica gel, molecular sieve 5A, and Porapak N. The total hydrocarbon analysis is directly sampled from a sample loop.

3. The fittings and plumbing are composed of 316 stainless steel, with valves of Teflon slide type, stainless steel base.

4. The air source is of zero-grade (99.99% purity). Hydrogen is generated from a hydrogen generator (99.9999% purity) and dried with a molecular sieve 5A trap prior to entry to the chromatograph.

3. Analysis of Sulfur Components

The determination of total sulfur, sulfur dioxide, hydrogen sulfide and methyl mercaptan in air samples are conducted utilizing a Tracor, Model 270 Sulfur Chromatograph.

A. Preparation of Chromatograph

1. Plug in the analyzer and push the power "on" button on the front of the analyzer.
2. Turn on the hydrogen source and establish 65 psi outlet pressure.
3. Check the compressed air outlet pressure is 80 psi and a 50-60 milliliter flowrate on the flowmeter on the front control panel.
4. Open the hydrogen control valve on the front panel and push the ignition button to light the flame ionization detector. Note the hydrogen pressure should be set to give a 55 cc/min flow rate.
5. Set the control knobs on the front panel to ambient sampling and automatic cycle.
6. Switch the range switch at the rear of the chromatograph to the appropriate range, 0-1 ppm or 0-200 ppb.
7. Attach the air sample bag to the ambient sample line and push the manual zero and recycle buttons to inject a sample into the chromatograph.

B. Calibrations

Calibrations conducted are tabulated in the Operational Log Book to be incorporated in the daily analysis of air bag samples.

1. Daily calibration

   a. Calibration is conducted using a Bendix Dynamic Calibration System, which consists of a NBS certified sulfur dioxide permeation tube.

   b. Total sulfur calibration is achieved using the sulfur dioxide response on the total sulfur mode of the chromatograph.

   c. Calibration is initiated by connecting the standard sample line to the permeation system and switching the sampling control knob to standard mode.

d. Press the manual zero and the recycle button to inject a sample from the permeation system.

e. The total sulfur response should appear in 7 seconds followed by hydrogen sulfide, sulfur dioxide and methyl mercaptan within the ten minute cycle period.

f. Calibration for H_2S and CH_3SH will be conducted at a later date when permeation tubes or standard gas mixtures are acquired.

2. Monthly Calibration

A monthly five-point calibration will be conducted to check linearity.

3. Periodic Calibration

Periodic calibrations every six months will include:

a. Linearity check of the 1 mv recorder

b. Functional check of pressure gauges and rotameters

C. Sample Analysis

1. Enter all pertinent data of the air bag sample in the Sulfur Operational Log Book.

2. Bag sample analyses are conducted in duplicate with the first sample repeated at the end of the day and the concentration of the four components determined to the ppb level by comparison of peak height response of the sample to the daily calibration curve.

D. Maintenance

Maintenance conducted will be logged in the Maintenance Log Book under the section headed Sulfur Chromatograph.

1. Adjust the electrometer for zero and set the high and low range chromatograph terminals to 1 mv every two weeks.

2. Set high and low linearizers at the same time as the electrometer adjustment.

3. Leak check the chromatograph every three months or as needed.

4. Regenerate the molecular sieve moisture traps once a month.

E. Hardware

1. The Tracor sulfur chromatograph consists of a dual mode analysis of total sulfur and the three sulfur compounds SO_2, H_2S, and $HSCH_3$. Sulfur compounds are determined with a flame-photometric detector utilizing a photo-multiplier and hydrogen rich flame ionization detector.

2. Connecting lines and fittings are nylon or 316 stainless steel.

3. Analysis columns are proprietary and are acquired directly from Tracor.

4. The hydrogen and air supply are zero grade 99.99% purity and are predried with molecular sieve driers.

4. Total Nitrogen Oxides Analysis

Total nitrogen oxides are determined utilizing a Bendix, Model 8101-B NO_x analyzer.

A. Preparation of analyzer

1. Turn on oxygen source and set the pressure regulator at 30 psi outlet pressure.

2. Turn on power switch to pump and analyzer.

3. Set oxygen source for ozone generator to 20 psi by opening valve on control panel.

4 Switch analysis mode knob to NO_X only.

5. Switch analysis valve switch to $NO-NO_2-NO_x$ position; mode switch to ambient; and the NO_x scale switch to 0.5 ppm.

6. Turn on the chart recorder, 10 millivolt full-scale.

7. Check the chamber pressure, minimal value of 23 inches Hg.

8. Connect air bag sample to inlet port on rear of the analyzer marked ambient air.

B. Calibrations

All calibrations are logged in the analysis book to be incorporated into sample analyses for that day.

1. Daily Calibration

Daily calibrations are conducted prior to sample analysis:

a. Connect the ambient air inlet line of the NO_x analyzer to the Bendix Dynamic calibrator.

b. Allow pure air to enter the NO_x analyzer and set the zero points for NO and NO_x using the appropriate zero knobs on the front of the analyzer.

c. Connect the quality control standard of 100 ppm NO in nitrogen gas to the inlet of the Bendix dilution system and establish a 400 ppb NO concentration by switching the appropriate dilution valves (consult the dilution curves for each valve).

d. Adjust the NO and NO_x span knobs to 80% of full scale.

e. Check the NO_2 convertors efficiency by switching the ozone generator, allowing part of the NO to be converted to NO_2, and checking to see if the NO_x value is the same as the NO_2 is converted back to NO.

f. Recheck the zero points with pure air for any deviation.

2. Periodic Calibration

Periodic calibrations are conducted monthly by:

a. Establishing a five-point calibration curve using the Dynamic Calibrator with the NO quality control standard. This will check the linearity, as well as, for leaks and errors in the gas concentration from the Dynamic Calibrator.

b. Verification of the NO concentration of the quality control standard by direct comparison to the NBS certified NO standard on the NO_x analyzer.

c. Establishing that sufficient moisture is in the zero air by checking for a zero off-set. This can be prevented with the use of oxygen, with 10 ppm moisture content, for ozone generation.

d. Determining the NO_2 content of the quality control standard by running a standard NO_x zero and span. Inside the analyzer interchange the NO inlet line to the control valves with the NO_x line entering the control valve from the reduction catalyst, allowing introduction of NO span gas with NO_2 impurity. If NO_2

is present, the NO_x span value will be lower than the previous span value, and the difference is a measure of the NO_2 present.

Instrument hardware checks will be made every six months, functionally checking the pressure gauges, valves, and 1mv recorder.

C. Sample Analysis

To perform sample analysis, enter all pertinent data into the NO_x Operational Log Book, then:

1. Connect the air sample bag to the ambient air inlet line of the NO_x analyzer.
2. Maintain the analyzer in the same concentration and operational mode as it was calibrated.
3. Allow the pen on the recorder to stabilize and read ppm NO_x directly by comparison to the span value set in calibration.
4. Nitric oxide will not be analyzed in the air sample bags due to thermal degradation of the sample during transfer to the laboratory.
5. First sample of the day is analyzed in duplicate at the end of the day.

D. Maintenance

Maintenance is logged in the Maintenance Log Book under the section for the NO_x analyzer.

1. Monthly replace the charcoal in the ozone scrubber on the back of the analyzer.
2. Conduct a leak check of the calibration system and NO_x analyzer when deviations in the daily zero or span exceeds 1% of previous values.

E. Hardware

All materials used in the NO_x analyzer are either Teflon or 316 stainless steel, including the connecting lines from the Bendix Dynamic Calibration system.

1. Air source used in calibration with the Dynamic Calibration system is discussed in the following sections.
2. The NO standard used in daily calibration is a nominal 100 ppm NO in nitrogen gas, and traceable to NBS.

3. The charcoal used in the ozone scrubber is activated cocoanut charcoal.

5. Halogenated Compound Analysis

Halogenated compounds of SF_6, fluorocarbon 11 and fluorocarbon 12 will be determined using an electron capture detector, Varian Model 940 gas chromatograp

A. Preparation of the chromatograph

1. Establish column flow rate at 30 ml/min nitrogen gas.

2. Check that column temperature is at ambient.

3. Determine standing current is above 2×10^{-8} amps.

B. Calibrations are conducted daily and logged in the Operational Log Book for the Varian Chromatograph.

1. Standards prepared in the laboratory are at the part per trillion concentration and are made from 99% purity fluorocarbon 11 and 12, SF_6 in hydrocarbon free air (± 10% accuracy).

C. Sample Analysis

1. Enter all pertinent data of the air bag sample in the Varian Operational Log Book.

2. Air samples are analyzed in duplicate and concentration to the nearest part per trillion determined for each compound.

3. The sample will be introduced with a valve system similar to that previously described for the Perkin-Elmer 900 Gas Chromatograph.

4. Concentration methods will be incorporated with samples where necessary.

D. Maintenance

Maintenance conducted is logged in the Maintenance Log Book under the section pertaining to the Varian Chromatograph.

1. Regeneration of the oxygen trap used with the nitrogen carrier.

2. Clean the radioactive foil every two months per instruction manual.

3. Conduct a leak check of the chromatograph when the foil is cleaned.

E. Hardware

1. The electron capture is a Scandium Tritide Foil (Sc^3H) of 1000 millicure radioactivity strength.

2. Carrier gas is oxygen free nitrogen of 99.99% purity.

3. The analysis column is constructed of 316 stainless steel, as well as the introduction valve system.

4. The oxygen trap is proprietary in nature and is purchased from Alltech Supplies.

6. Bendix Pure Air System

The Bendix Pure Air System is designed to supply pure, moisture-free air to the Dynamic Calibration system. This is achieved by compressing ambient air, converting NO impurity to NO_2 with an ultraviolet light source, and subsequent adsorption of the NO_2 and other impurities on charcoal. The free air is then dried by passing through a silica gel trap and filtered prior to entering the Dynamic Calibration system.

A. Operational Procedure consists of plugging the power cord into an electrical outlet and switching "ON" the ultraviolet light source.

B. Maintenance performed will be logged in the Maintenance Log Book under the section for Dynamic Calibration System.

1. Once a week the surge tank should be drained of excess water.

2. The charcoal and silica gel adsorbants should be changed once a month if the system is connected to the laboratory air system; otherwise, once a week when room air is used.

3. The ultraviolet light source is changed whenever NO is found in the zero air used to zero the NO_x analyzer.

C. Hardware is composed of activated cocoanut charcoal, 6 to 14 mesh; indicating silica gel, grade 42, 6 to 16 mesh; and dust trap of fine grade fiberglass wool.

7. Bendix Dynamic Calibration System

The Bendix Dynamic Calibration System is used in conjunction with the NO Quality Control Standard and a NBS certified SO_2 permeation tube to provide part per billion level calibration gases for the NO_x and sulfur analyzers. The calibration gases are established by the dilution of pure gas through a capillary system with pure air from a Bendix Pure Air System.

A. Preparation of the Calibration System.

1. Connect the Bendix Pure Air System to the inlets A and C of the Dynamic Calibrator.
2. Attach the NO quality control standard to the inlet B of the calibrator.
3. Attach the permeation tube vent line and the dilution system vent line to the room air vent.
4. Connect the output of the calibration system to the analyzer to be calibrated.
5. Turn the switches on the front panel for the particular gas to be diluted, either NO or the SO_2 permeation system.

B. Calibration

1. Each of the seven flow regulating capillaries are calibrated every three months by plotting flow rate versus pressure applied to a given capillary. The flow rates are determined with a bubble flowmeter and are cross-checked periodically with a mass flowmeter.
2. The constant temperature bath that houses the SO_2 permeation tube, is checked for accuracy at the same time the capillaries are calibrated.
3. Pressure gauges are functional checked every six months.

C. Operational Procedure

1. Once the calibration system has pure air flow, the desired concentration is achieved by connecting the desired concentrated source of NO or SO_2 to the capillary network.
2. The NO span gas is obtained by adjusting the air pressure in Section B and activation of the toggle valve to permit the NO to flow to the capillary system.
3. The ppb NO span gas is achieved by switching the various toggle valves to divert the NO gas through the individual capillaries. Reference to the calibration curves for each capillary will indicate what concentration to expect.
4. The SO_2 span gas is obtained in a similar manner by switching the vent valve to connect Section A to the capillary section. The flow rate is established by adjusting air pressure and

switching the toggle switch for high or low flow rates.

5. The dilution gas desired is obtained, as before, with the selection of which capillary to use.

6. Multipoint calibration can be achieved for either SO_2 or NO by choosing the proper combination of capillaries at a constant pressure setting.

D. Maintenance

Maintenance is performed and logged in the Maintenance Log Book under the section pertaining to the Dynamic Calibration System.

1. A leak check of the calibration system will be conducted every three months.

E. Hardware

Material used in the Calibration System is either Teflon or 316 stainless steel.

1. The SO_2 permeation tube is NBS certified to 1.503 micrograms/min permeation rate at 25° C.

2. The NO standard cylinder is acquired from Airco Gas Co. at nominal 100 ppm NO in nitrogen gas and certified with a NBS NO standard.

8. General Procedures

A. RAMS Sample Bag Leak Checks

A leak check of Teflon bags used in sampling at the RAMS sites is performed routinely before each use.

1. Initially, all new Teflon bags received are assigned a serial number and filled with dry air for a leak test.

2. The bags are filled to 80% capacity and capped off.

3. A book (approx. 1/2 lb.) is placed on the bag and left over-night to check for leaks.

4. If the bag is leak-proof, it is purged with high-purity helium repeatedly and stored for use in sampling.

5. If the bag is found to leak, it is filled with high-purity helium and capped.

6. Using a Gow-Mac leak detector, which compares the thermoconductive of reference air to helium, the bag is leak checked.

7. If practical, identified leaks are sealed with a Weldron bag sealer and leak check is initiated again with the bag filled with air.

B. Laboratory Gas Standards

Calibration checks using gas standards made up in the laboratory are prepared as follows:

1. The primary zero air standard consists of zero air with purity of <0.1 ppm CH_4, CO, and NO_x, and <0.01 ppm SO_2.

2. Standards are made up in the zero free air or of known purity with pure gases of minimum purity of 99.0%.

3. Volume measurements of the air is determined with a Precision Scientific Wet Test Meter (± 0.5% volume) accuracy.

4. Volume measurements of pure gases are with precision gas tight syringes (Hamilton, Precision Scientific, etc.)

C. Quality Control Standards

1. PE900 - laboratory prepared gas mixtures of pure hydrocarbons in hydrocarbon free air, contained in a 22 liter steel cylinder @ 200# pressure. Concentration is verified by repetitive analysis with gas standards for each individual hydrocarbon.

2. Beckman 6800 - a mixture of 5ppm CO and CH_4 in air, and two other gas standards of 8 ppm CH_4 in Air and 15 ppm CO in Nitrogen, will be used for calibration (± 1% accuracy), and concentrations are verified by NBS certified gas standards.

3. Sulfur Chromatograph - NBS certified SO_2 permeation tube (accuracy of ± 1.0%).

4. Bendix NO_x Analyzer - use of an Airco NO gas standard in nitrogen gas, which is certified with an NBS certified NO in nitrogen gas standard (± 1.1% accuracy).

3.0 DATA PROCESSING

Data generated by the RAPS Gas Chromatography Laboratory is processed and entered into the RAPS Computer Data Bank, Research Triangle Park (RTP), North Carolina. Data processing from analysis to final residence in the data bank is performed as follows:

1. Data Tabulation

It is planned to perform approximately twenty analyses per week for up to 126 components. When performing these analyses, as described in the preceding section, the data is initially recorded in the form of strip chart chromatograms, punch tape and/or teletype printouts. Next, the data is given one of its first quality reviews by manually inspecting the data for general chromatograph form factors and quantitative values for each gas component. Following review and approval, the data is then tabulated on a special pre-printed form for keypunching (inclusive as Figure 14).

2. Keypunching and Processing

At the end of approximately a ten-day collection period, the data forms are sent to Research Triangle Park for keypunching and keypunching validation. The cards are then shipped to the RAMS Central Computer Facility, St. Louis, for processing and further validation. Keypunching errors will normally be corrected by computer operators at the RAMS Computer Facility, provided they are not excessive. Should a significant quantity of keypunch errors develop that the RAMS computer operators cannot process in their normal schedule, the card decks and data sheets will be returned to RTP for repunching.

Data processing entails checking the cards for index number consistency, as provided for by the form, and then producing a triple copy printout of labeling information, and for each component the name, code number, concentration (PPB), ratio relative to CO, and flags if the concentration or ratio is outside an upper and lower set of limits as provided by EPA. Four quantities, aggregated by software, are treated as components in all respects: sum of non-methane paraffins, olefins, aromatics, and non-methane hydrocarbons. Validation of the data concludes upon successful visual inspection and comparison of the data with the chromatogram and original tabulated data. Also, special attention will be directed to flagged data for validity and proper annotation.

Upon completion of data validation, a 600 foot, 9 track, 800 BPI, odd-parity magnetic data tape is prepared and sent to RTP, along with a copy of the printout. One copy of the remaining two printouts is sent to the EPA Raps Task Order Coordinator (St. Louis) and the third copy retained by the RAMS Central Computer Facility.

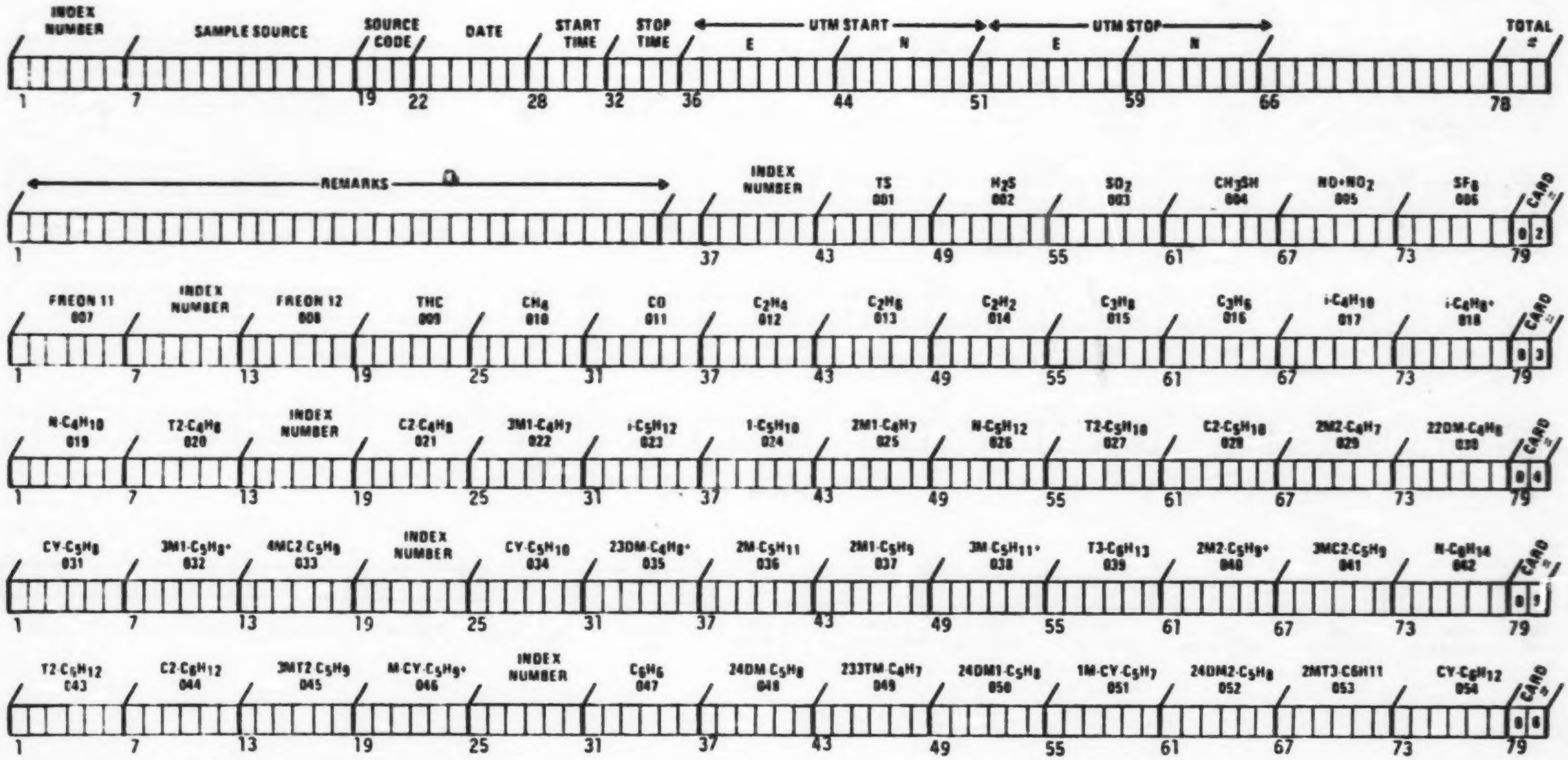
INDEX NUMBER
SAMPLE SOURCE
SOURCE CODE
DATE
START TIME
STOP TIME
UTM START
E
N
UTM STOP
E
N
TOTAL #
1
7
19
22
28
32
36
44
51
59
66
78
REMARKS
INDEX NUMBER
TS 001
H_2S 002
SO_2 003
CH_3SH 004
$NO+NO_2$ 005
SF_6 006
CARD #
0 2
1
37
43
49
55
61
67
73
79
FREON 11 007
INDEX NUMBER
FREON 12 008
THC 009
CH_4 010
CO 011
C_2H_4 012
C_2H_6 013
C_2H_2 014
C_3H_8 015
C_3H_6 016
i-C_4H_{10} 017
i-C_4H_8* 018
CARD #
0 3
1
7
13
19
25
31
37
43
49
55
61
67
73
79
N-C_4H_{10} 019
T2-C_4H_8 020
INDEX NUMBER
C2-C_4H_8 021
3M1-C_4H_7 022
i-C_5H_{12} 023
1-C_5H_{10} 024
2M1-C_4H_7 025
N-C_5H_{12} 026
T2-C_5H_{10} 027
C2-C_5H_{10} 028
2M2-C_4H_7 029
22DM-C_4H_8 030
CARD #
0 4
1
7
13
19
25
31
37
43
49
55
61
67
73
79
CY-C_5H_8 031
3M1-C_5H_8* 032
4MC2-C_5H_9 033
INDEX NUMBER
CY-C_5H_{10} 034
23DM-C_4H_8* 035
2M-C_5H_{11} 036
2M1-C_5H_9 037
3M-C_5H_{11}* 038
T3-C_6H_{13} 039
2M2-C_5H_9* 040
3MC2-C_5H_9 041
N-C_6H_{14} 042
CARD #
0 5
1
7
13
19
25
31
37
43
49
55
61
67
73
79
T2-C_5H_{12} 043
C2-C_6H_{12} 044
3MT2 C_5H_9 045
M-CY-C_5H_9* 046
INDEX NUMBER
C_6H_6 047
24DM C_5H_8 048
233TM-C_4H_7 049
24DM1-C_5H_8 050
1M-CY-C_5H_7 051
24DM2-C_5H_8 052
2MT3-C6H11 053
CY-C_6H_{12} 054
CARD #
0 6
1
7
13
19
25
31
37
43
49
55
61
67
73
79

FIGURE 14

GAS CHROMATOGRAPHY LABORATORY DATA SHEETS

4M1-C_6H_{11}* 055	3M2E1-C_6H_8* 056	CY-C_6H_{10} 057	2M-C_6H_{13}* 058	23DM-C_5H_{10}* 059	INDEX NUMBER	3M-C_6H_{13} 060	C13DM-CY-C_5H_8* 061	2E1-C_5H_9* 062	3E-C_5H_{11}* 063	224TM-C_5H_9* 064	C3-C_7H_{14} 065	3MC3-C_6H_{11}* 066	CARD # 0 7
1	7	13	19	25	31	37	43	49	55	61	67	73	79

3E2-C_5H_9 067	N-C_7H_{16} 068	23DM2-C_5H_8* 069	C12DM-CY-C_5H_8 070	M-CY-C_6H_{11}* 071	4M-CY-C_6H_{11} 072	INDEX NUMBER	25DM-C_6H_{12} 073	E-CY-C_5H_9 074	24DM-C_6H_{12} 075	223TM-C_5H_9 076	C,T-TM-CY-C_5H_7 077	TOLUENE * 078	CARD # 0 8
1	7	13	19	25	31	37	43	49	55	61	67	73	79

234TM C_5H_9 079	233TM C_5H_9 080	23DM C_6H_{12}* 081	2M-C_7H_{15} 082	4M-C_7H_{15} 083	34DM C_6H_{12}* 084	3M-C_7H_{15}* 085	INDEX NUMBER	225TM-C_6H_{11}* 086	T14DM-CY-C_6H_{10} 087	1MT3E-CY-C_5H_8 088	224TM-C_6H_{11} 089	CY-C_7H_{14}* 090	CARD # 0 9
1	7	13	19	25	31	37	43	49	55	61	67	73	79

T12DM CY C_6H_{10}* 091	N C_8H_{18} 092	T13DM CY C_6H_{10} 093	224TM C_6H_{11} 094	235TM C_6H_{11} 095	22DM C_7H_{14} 096	24DM C_7H_{14}* 097	2M4E C_6H_{12}* 098	INDEX NUMBER	26DM-C_7H_{14}* 099	N-PR-CY-C_5H_9 100	E-CY-C_6H_{11} 101	25DM-C_7H_{14}* 102	CARD # 1 0
1	7	13	19	25	31	37	43	49	55	61	67	73	79

E C_6H_5 103	33DM C_7H_{14} 104	233TM C_7H_{13} 105	P XYL 106	M XYL 107	4M C_8H_{17} 108	2M C_8H_{17} 109	3E C_7H_{15} 110	3M-C_8H_{17} 111	INDEX NUMBER	O XYL 112	224TM-C_7H_{13} 113	225TM-C_7H_{13}* 114	CARD # 1 1
1	7	13	19	25	31	37	43	49	55	61	67	73	79

225TM C_7H_{13}* 115	N-C_9H_{20} 116	N PR C_6H_5 117	2233TM C_6H_{10} 118	1M2E C_6H_4 119	135TM-C_6H_3 120	TER BU C_6H_5 121	124TM C_6H_{13} 122	SEC-BU-C_6H_5* 123	N-$C_{10}H_{22}$ 124	INDEX NUMBER	123TM-C_6H_3* 125	N BU-C_6H_5 126	CARD # 1 2
1	7	13	19	25	31	37	43	49	55	61	67	73	79

FIGURE 14 (CONTINUED)

GAS CHROMATOGRAPHY LABORATORY DATA SHEETS

4.0 QUALITY ASSURANCE

Final application of data from the Gas Chromatography Laboratory in the RAPS study and model development is highly dependent upon the quality and validity of the data. Analysis methodologies and calibration procedures must be established to insure that the highest quality data is compiled commensurate with budgetary and technical constraints. In this light, a quality assurance program has been established to provide meaningful data.

1. Instrumentation System

The instrumentation selected and provided by the EPA for use in the Gas Chromatography Laboratory was made to provide the latest, most accurate, and dependable systems possible. Operational procedures have been developed for every instrument to insure its maximum performance. To insure that high-quality data is generated by the laboratory, all instruments are subjected to preventative maintenance and repair, both routinely and as required. A detailed description of all maintenance performed, both routine and unscheduled, is entered in the laboratory, (also described in the previous instrument sections of this Work Plan).

Data accuracy is assured by performing both daily detailed and monthly general instrument calibration with the quality control standards discussed in the previous sections. The results of calibrations are entered in the Operational Log Book for each instrument along with the sample analysis for that day. To check repeatibility of the instrumentation, one of the bag samples will be analyzed in duplicate before and after each set of samples. This verification, along with daily calibration, will provide a check for variations in instrument parameters (such as, temperature, pressure, flow rate, etc.). A periodic cross-check between different instruments is frequently made using the quality control gas standards. An independent auditing check of the sample analysis is conducted weekly by the EPA Project Officer to spot check the data reported.

5.0 LABORATORY OPERATING SCHEDULE

For the laboratory to best serve the program objectives, it must be flexible in its operation. Periods of heavy analysis must be accommodated as well as days of light analysis. Also, the laboratory must be prepared and staffed to accommodate other related functions; such as, equipment maintenance, special testing, instrument modifications and calibrations. The laboratory staff must also perform various administrative functions, such as, purchasing and report writing. With this in mind, a laboratory capability has been established based upon the equipment identified earlier and a full-time staff of two and one-half personnel. With this staff the laboratory is designed to perform an average of twenty analyses per week. This figure can vary, depending upon the type of analysis to be run and how much analysis effort is required. To estimate the laboratory normal capabilities, the following work schedule is developed for each specific analysis and non-analysis work task. These time estimates do not include sample pick-up at the various RAMS stations or other sources.

	Man-hours	Man-hours per Week -- Total
1. General Laboratory Requirements - Other than Sample Analysis:		
A. Maintenance of Equipment	8	
B. Leak test and cleaning of sample bags; cleaning shall consist of two purgings of the bag after each use; with a total hydrocarbon check after four samplings with the bag. 0.20 hr/bag x 2 bags/wk.	4	
C. Report writing, seminars, etc. Average of 30 hrs/month	7	19
2. Labor Requirements for Chemical Analysis of Air Samples:		
A. Hydrocarbon analysis - C_2 to C_{10}, using two chromatographic columns for the total analysis		
1. A column for C_1 to C_4 hydrocarbons		
2. A column for C_3 to C_{10} hydrocarbons		
3. Calibration - quantitative on those days of sampling twice/week x 1.5 hrs.	3	
4. Sample analysis - simultaneous analysis of a sample on two columns, 1.0 hrs/sample x 20 samples/week	20	
5. Data reduction of analysis 0.25 hrs/sample x 20 samples/week	5	28
B. Hydrocarbon and carbon monoxide analysis with 6800 Chromatograph		
1. Calibration - quantitative with two gas mixtures each of methane in air and carbon monoxide in nitrogen. Twice/week x 0.5 hrs./check	1	
2. Sample analysis shall consist of a replicate analysis of total hydrocarbons and single analysis for methane and carbon monoxide per	10	

(cont'd.)

	Man-hours	Man-hours per Week -- Total
(Cont'd.) sample; including data reduction 0.5 hours/sample x 20 samples/wk.		
		11
C. Sulfur Component Analysis		
1. Calibration-using permeating system total sulfur and SO_2 on the day of sampling 1 hr/day (if total sulfur SO_2, H_2S, and CH_3SH on the day of sampling 2 hrs/day).	1	
2. Sample analysis will consist of three analysis per sample plus data reduction 240 samples over 40 weeks + 6 samples per week - 0.45 hrs/sample x 6	4.5	
		5.5
D. NO_x Analysis		
1. Calibration-on the day of sampling 1 hr/day x twice/week	2	
2. Sample analysis and Data reduction consisting of only NO_x analysis 0.25 hrs/sample x 20 samples/week	5	
		7
E. Halogenated Compound Analysis		
1. Calibration-made up daily and analyzed 1 hr/day x twice/week	2	
2. Sample analysis and data reduction, composed of analysis of SF_6, fluorocarbons 11 and 12 240 samples over 40 weeks = 6 samples/wk 0.5 hours/sample x 6 samples	3	
		5
F. Data Conversion to Magnetic Tape		
Considered as the tabulation on one sheet of all the analysis of a sample 1 hr/sheet x 20 samples	20	
		20

3. Estimate of Weekly Analysis Combinations:

A. Example 1

A week consisting of twenty samples analyzed for:

	Man-hours	Man-hours per Week -- Total
1. Hydrocarbon analysis -C_2 to C_{10}	23	
2. 6800 analysis	11	
3. NO_X analysis	7	
4. Sulfur components analysis (6 samples per/week)	5.5	
5. Halogenated compounds analysis (6 samples per/week)	5	
6. Data conversion to magnetic tapes	20	
7. General labor requirements	19	
		90.5

B. Example 2

Assuming two analyses running simultaneously (e.g., 50% operator time on 900 analysis and 25% each on any two of the other four analyzers).

	Man-hours	Man-hours per Week -- Total
1. Hydrocarbon analysis-C_2 to C_{10}	11.5	
2. 6800 analysis	5.5	
3. NOx analysis	3.5	
4. Sulfur components analysis (6 samples per week).	5.5	
5. Halogenated compounds analysis (6 samples per week).	5	
6. Data conversion to magnetic tapes	20	
7. General labor requirements	19	
		70